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Long-Term Effect of Vitamin E on Free Radicals and Thermouminescence Properties of Medical-Grade UHMWPE

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LONG-TERM EFFECTS OF VITAMIN E ON FREE RADICALS AND THERMOLUMINESCENCE PROPERTIES OF MEDICAL-GRADE UHMWPE

by

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Dedication

I would like to dedicate this thesis to my beloved family without whom none of my success would be possible.

I Love You.

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Long-Term Effects of Vitamin E on Free radicals and Thermoluminescence Properties of Medical-Grade UHMWPE

Abstract

This research project focuses on the effects of vitamin E on free radicals and thermoluminescence of 10-years old shelf-stored samples with different concentrations of vitamin E. Two spectroscopy methods were used to analyze the behavior of the free radicals in presence of vitamin E in old samples, Electron Spin Resonance (ESR) spectroscopy and Thermally Simulated Luminescence (TSL) spectroscopy. The experiments were performed on three different groups of UHMWPE. One group of samples includes vitamin E doped samples and non-vitamin E samples, both non-irradiated, which were stored in open air at room temperature (23°C) for more than 10 years. In this group, samples got irradiated with X-ray after 10 years of shelf-storage. In the second group of samples, vitamin E containing GUR 1020 solid samples were γ irradiated (30 kGy) more 10 years ago and have been stored in open air at room temperature (23°C). In the last group, non-irradiated samples doped with vitamin E and also non-irradiated non-vitamin E samples were forced to oxidized using thermal oxidation. Then samples were tested with TSL spectrometer. ESR analysis was performed using an in-house created software and TSL analysis was performed using PeakFit v4. The ultimate goal of this research project is to determine the long-term effects of vitamin E upon the production of free radicals during sterilization with γ-ray and X-ray. In addition, another objective is to determine whether or not vitamin E had any anti-oxidation effect on the free-radical induced oxidation of sterilized UHMWPE during shelf-storage in a room environment, after a long time (more than 10 years).

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Chapter 1

Introduction

1.1 Overview

Ultra-high molecular weight polyethylene (UHMWPE) is a biomaterial used as a bearing component in total-joint implants. It has extremely high molecular weight, low degree of crystallinity, high tensile strength, high impact resistance and chemical inertness. While some drawbacks such as creep may limit the application of UHMWPE, many research studies have been carried out to improve the mechanical properties of medical grade UHMWPE [1].

Irradiation has been proven to be a reliable and effective method for crosslinking and sterilization of UHMWPE. The crosslinking of polyethylene (PE) is achieved by the recombination of free radicals created by the high energy irradiation. Some free radicals might become trapped in the crystalline phase and initiate oxidation within the UHMWPE components by reacting with diffused oxygen, and therefore lead to degradation. However, vitamin E (α-tocopherol) added to UHMWPE has been found to improve oxidation resistance of UHMWPE by scavenging free radicals [2].

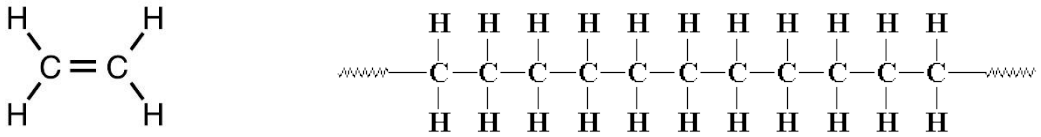
The primary reason for failure of implants made out of UHMWPE is the wear of the UHWMPE components. This wear is primarily due to oxidation, wich occurs slowly over time, and may be limited by the addition of vitamin E to the UHMWPE components. As free radical content can be considered as indicators to potential oxidation, it is important to study free radicals in UHMWPE and how they change over time in the long run, as well as effects that vitamin E may have on such free radical activity.

1.2 Ultra-High Molecular Weight Polyethylene (UHMWPE)

A polymer is a large molecule, or macromolecule, composed of many repeated subunits. Because of their broad range of properties, both synthetic and natural polymers play very significant roles in everyday life.

Polyethylene is a polymer formed from ethylene (C_2H_4), which is a gas having a molecular weight of 28, and the most popular plastic in the world. It is the polymer that makes grocery bags, shampoo bottles, children's toys, and even bulletproof vests. For such a versatile material, it has a straightforward structure, the simplest of all commercial polymers.

The generic chemical formula for polyethylene is $-(C_2H_4)_n-$, where n is the degree of polymerization. Figure 1.1 shows a schematic of the chemical structure of ethylene and polyethylene.



Ethylene Polyethylene

Figure 1.1 A schematic of the chemical structure of Ethylene and Polyethylene.

There are several kinds of polyethylene that are synthesized with different molecular weights and chain architecture. Sometimes some of the carbons, instead of having hydrogen atoms attached to them, will have long chains or branches of polyethylene attached to them. It is called branched, or low-density polyethylene, or LDPE, with a molecular weight of typically less than 50000 g/mol.

When there is no branching, it is called linear polyethylene, or HDPE (high-density polyethylene). Its molecular weight can be up to 200000 g/mol. Linear polyethylene is much stronger than branched polyethylene, but branched polyethylene is cheaper, easier to make, and more flexible.

Polyethylene with molecular weights of 3,000,000 to 6,000,000 g/mol is referred to as ultra-high molecular weight polyethylene or UHMWPE. It can make fibers which are so strong in a way that they can be used in bulletproof vests. Large sheets of it can be used instead of ice for skating rinks. The molecules of UHMWPE are several orders of magnitude longer than those of familiar high-density polyethylene (HDPE).

UHMWPE has frequently been served as the acetabular cup of the artificial hip joint (AHJ) since it combines superior wear resistance along with high fracture toughness and biocompatibility compared to other polymers [2].

1.2.1 Structure and Properties of UHMWPE

UHMWPE has outstanding physical and mechanical properties such as high abrasion resistance, high impact toughness, excellent corrosion and chemical resistance, resistance to cyclic fatigue, and resistance to radiation, which make it ideal for use in orthopedic components. It embodies all the characteristics of high-density polyethylene (HDPE) with the added traits of being resistant to concentrated acids and alkalis as well as numerous organic solvents. It is odorless, tasteless, and nontoxic. It is highly resistant to corrosive chemicals, has extremely low moisture absorption and a very low coefficient of friction [3]. Table 1 compares the mechanical properties of HDPE and UHMWPE.

Table 1 - Physical and Mechanical Properties of HDPE and UHMWPE [4]

Property	**HDPE**	**UHMWPE**
Molecular weight (10^6 g/mol)	0.05-0.25	3.5-7.5
Melting Temperature (°C)	130-137	132-138
Tensile modulus of elasticity (GPa)	0.4-4.0	0.5-0.8
Tensile Ultimate strength (MPa)	22-31	39-48
Impact strength (J/m)	21-214	>1070 (no break)

Ultra-high Molecular Weight Polyethylene has a composite structure with highly ordered crystalline lamellae embedded in a randomly oriented amorphous matrix.

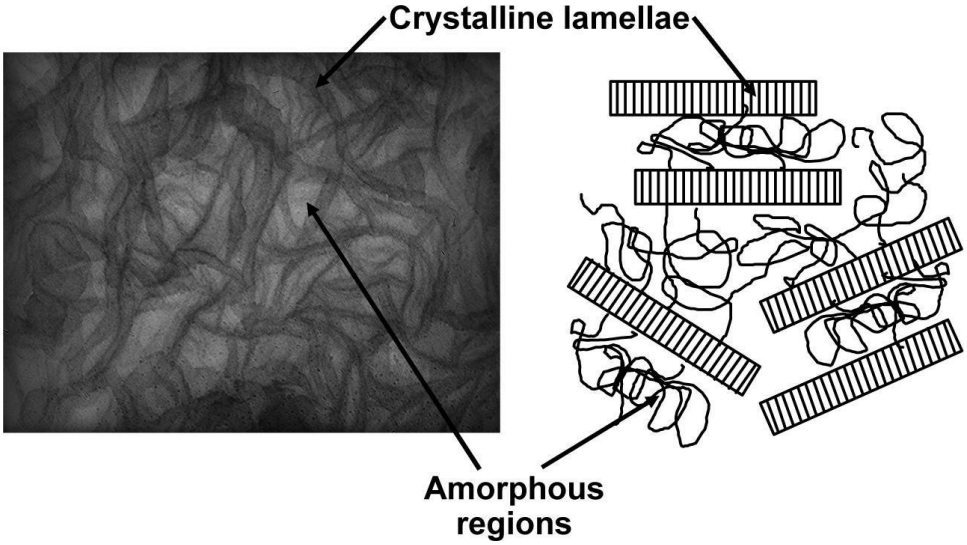


Figure 1.2 The crystalline lamellae embedded in an amorphous matrix.

It is well known that the mechanical properties and oxidative stability of UHMWPE are affected by the irradiation dose, resin type, and post-irradiation heat treatment, among other factors. Therefore, careful consideration of these variables should be made for a given application.

1.2.2 Ethylene Gas to UHMWPE Powder

The UHMWPE powders have been produced By Ruhrchemie company using Zeigler process. Ethylene (a reactive gas), hydrogen, titanium tetra chloride (a catalyst), and calcium stearate (additive act as scavenger for residual catalyst) are the main ingredients of HUMWPE. During polymerization, the catalyst produces trace impurities of titanium, aluminum and chlorine, which are minimized by additive calcium stearate. The trace levels of calcium stearate and the ash content depend on the storage and handling of the powder after polymerization. The polymerization takes place in a solvent used for mass and heat transfer [2].

1.2.3 UHMWPE: From Powder to Consolidated Form

The consolidation process of UHMWPE requires the proper combination of temperature, pressure and time since it does not flow like lower molecular weight polyethylene when raised above its melt temperature. Compression molding, ram extrusion, and hot isostatic pressing are typical conversion methods to produce commercially available consolidated UHMWPE. A machining step is required to shape the consolidated UHMWPE into orthopedic implant components, except for the direct compression molding technique. The UHMWPE components for total joint replacements are then packaged and sterilized before distribution to the external market [2].

GUR Resin (Two types: GUR 4150 and GUR 4120) and 1900 Resin (Designated as Himont 1900 or Hylamer) are two major types of medical grade UHMWPE which are commonly consolidated to form UHMWPE components of artificial hip and knee joint replacements [2].

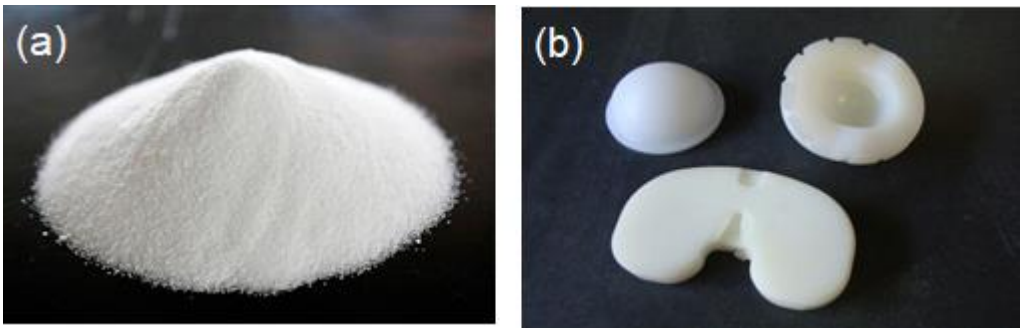


Figure 1.3 UHMWPE (a) Powder Form, (b) Consolidated Form (as Hip and Knee Implants)

1.2.4 GUR Resin versus 1900 Resin

The trace level of residuals and ash contents during polymerization is one way to explain the differences between GUR and 1900 resins. The product requirements for both type of resin specified by American Society for Testing and Materials (ASTM) standard F648 and ISO standard 5834-1 are shown in Table 2.

Table 2 - Requirements for Medical-Grade UHMWPE Powders [2]

Property	**Requirements**	
Trade name	GUR 1020 and 1050	1900 H
Ash, mg/kg, (maximum)	125	300
Titanium, ppm, (maximum)	40	150
Aluminum, ppm, (maximum)	20	100
Calcium, ppm, (maximum)	5	50
Chloride, ppm, (maximum)	30	90

There is another way to distinguish two major resins of UHMWPE, GUR resin and 1900 resin, such as average resin particle size, the size distribution, and morphology of the resin particles [6].

Table 3 - Comparison of Physical Properties of GUR and 1900 Resins

Resin Designation	Average Molecular Weight, ASTM Calculation (10^6 g/mol)	Morphology	Average Particle Size (μm)
GUR	3.5-6	Lamellar crystalline	140
1900H	> 4.9	Spherulitic crystalline	300

The differences mentioned here can cause different behavior in mechanical properties (such as impact strength); they also cause the formation of primary radicals upon gamma irradiation, the recombination of radicals, and the long-term oxidation reaction of residual radicals.

1.2.5 GUR Resin

The company Celanese (formerly known as Ticona, and before that as Ruhrchemie) has designated GUR to its UHMWPE grades, in which the acronym GUR stands for “Granular”, “UHMWPE”, and “Ruhrchemie”. There are different grades of GUR, such as 4150, 1150, 1050, 1120, and 1020. The first digit of the grade number represents the loos bulk density of the resin, which is the weight measurement of a fixed volume of loose unconsolidated powder. To clarify, the digit “4” in GUR 4150 means that the bulk density of the resin is over 400 g/L. The second digit is an indication of presence (1) or absence (0) of calcium stearate. The third digit corresponds to the average molecular weight of the resin, while the fourth digit is an internal code designation.

1.3 Sterilization

Before implantation into the body, UHMWPE must be sterilized to prevent contamination. It can be done using ethylene oxide or high-energy radiation (electron beam, X-ray or γ irradiation). The ionizing radiation of UHMWPE can be performed on the material for two different purposes: irradiation to sterilize the material and irradiation to modify or improve some mechanical properties [7].

The process of oxidative degradation begins with the sterilization of the polymer by X-ray or γ irradiation. The high energy photons deposit energy in the polymer, which can result in the breaking of the C-H bonds [8]. Irradiating UHMWPE with ionizing radiation causing free radicals to form throughout the irradiated volume.

1.4 Free Radicals

Free radicals are atoms or groups of atoms with an odd (unpaired) number of electrons or with unpaired electrons. Once formed, these highly reactive radicals can start a chain reaction, like dominoes. They usually attack neighboring molecules causing the

affected molecules to become free radicals themselves. The new free radicals attack the next stable molecules and a chemical chain reaction of radical production occurs.

Typically, our body can handle free radicals using antioxidants. However, if antioxidants are not available in the body, or if the free-radical production becomes excessive, damage can occur. Free radicals are primary agents of oxidation. They get oxidized inside the human body and cause a range of disorders including cancer, arthritis, diabetes, and aging.

Along with the crosslinking in the amorphous phase of the UHMWPE, irradiation also initiates the formation of free radicals in the crystalline phase. These free radicals can reside in the crystalline, amorphous, or interfacial regions. The radicals in the amorphous regions have the potential to oxidize, while the radicals in the crystalline regions are shielded from immediate oxidation [12]. The residual free radicals (from the crystalline regions) will migrate to the crystalline/amorphous interface and cause oxidative degradation in the material through the reactions with oxygen [9].

1.4.1 Free radicals in UHMWPE

In the literature, frequently reported primary free radicals for UHMWPE, which are produced as a result of irradiation are as follows:

Alkyl: —CH_2—•CH—CH_2

Allyl: —CH_2—CH=CH—•CH—CH_2— or —CH_2—•CH—CH=CH—CH_2—

Polyenyl: —CH•—H$(CH=CH)_n$—

Figure 1.4 represents the Electron Spin Resonance (ESR) spectra of the primary radicals produced in UHMWPE as a result of irradiation.

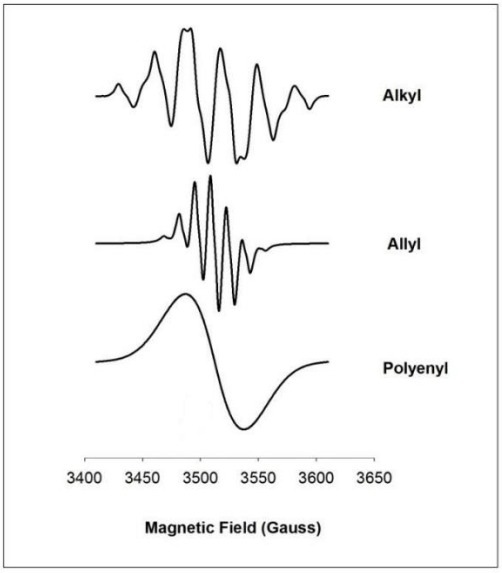


Figure 1.4 ESR spectra of primary free radicals of UHMWPE.

The primary radicals can be recombined over time, if the polymer were stored in air. However, some trapped radicals in the crystalline region could convert to short-lived secondary or tertiary radicals, which causes the oxidation process in UHMWPE [10].

The secondary or tertiary radicals are:

Peroxy: —CHO_2•—

Alkoxy: —CHO•—

Vinyl: >CH=•CH_2—

1.5 Improvements of UHMWPE as an Orthopedic Material

In the past 50 years, there have been many attempts to improve the mechanical properties and lifetime of the polymer. In early 1900s, due to clinical concerns, a research on the relationship between UHMWPE structure, mechanical properties and wear performance led to an increased interest on cross-linking for the polymer. Cross-linking is achieved by irradiation. However, the irradiation process produces free radicals. Some of the free radicals get quenched during the cross-linking, but there would be some residual free radicals in the polymer [2]. To effectively quench the residual free radicals, it was suggested to heat the polymer above its melting temperature.

A combination of radiation cross-linking and thermal treatment emerged in late 1990s as a technology to improve the wear and oxidation resistance of the polymer [2]. The development of this technology has led to a series of new alternates UHMWPE bearing materials, such as irradiation and melting, irradiation and annealing, sequential irradiation with annealing, and irradiation and stabilization with vitamin E.

1.6 Antioxidants

It's widely accepted that all organic polymers will degrade when exposed to certain environmental conditions such as high temperatures, mechanical shear, and high-energy radiation. The presence of oxygen will accelerate this degradation. Antioxidants are used to retard the oxidation reaction of the polymers. Antioxidants are intimately involved in the prevention of cellular damage; the common pathway for cancer, aging, and a variety of diseases. Oxidation is a chemical reaction caused as a result of free radicals existence and will damage the cells. Antioxidants terminate these chain reactions. They are molecules which can safely interact with free radicals and terminate the chain reaction before vital molecules are damaged.

Vitamin E is an effective biological antioxidant, helping to prevent the oxidative degradation of cell membrane phospholipids. When added to UHMWPE, vitamin E performs a similar role, helping to avoid the oxidation of the polyethylene chains [9]. There are other synthetic antioxidants which has been reported to be blended with UHMWPE, such as synthetic Phenolic Antioxidants. However, vitamin E is still the most popular and most promising antioxidant due to its biocompatibility and the oxidation resistance it adds to the polymer.

1.6.1 Vitamin E

The main issue to improve mechanical properties of orthopedic implants is to decrease oxidation degradation. To put in other words, developing ways in order to produce more oxidation-resistant UHMWPE is the ultimate goal. An alternative method to do so is the stabilization of the radiation-induced free radicals by using an antioxidant [11].

The idea of blending vitamin E with UHMWPE as an antioxidant is not new. In the first place, Luigi Costa reviewed how oxidation process may be effectively blocked with an appropriate antioxidant recommended vitamin E. Vitamin E was recommended as a likely candidate for use in orthopedic UHMWPE because it's obviously biocompatible and is approved as antioxidant for food packaging.

Vitamin E (α-tocopherol) has been proven to improve the oxidation resistance and fatigue strength of irradiated UHMWPE [11]. Vitamin E donates hydrogen to free radicals of UHMWPE in order to stabilize them. In this process, vitamin E becomes a free radical itself (tocopheryl radical) although it's more stable relative to radicals of UHMWPE. Figure 1.5 shows the structure of the vitamin E (α-tocopherol) molecule and its radical.

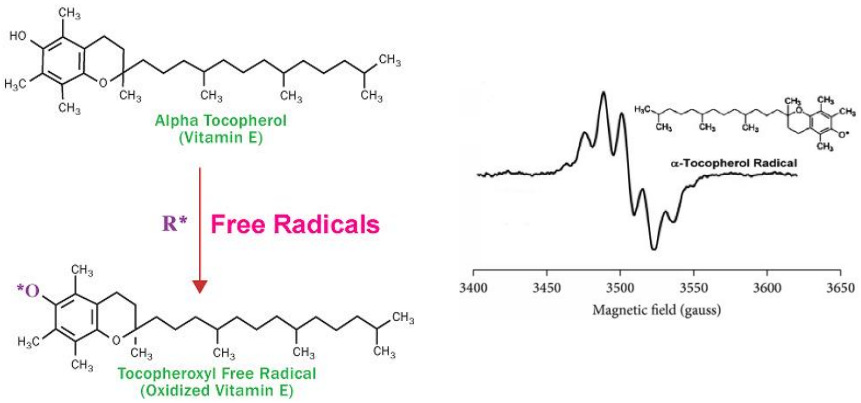


Figure 1.5 (a) Molecular Structure of α-Tocopherol and α-Tocopherxyl radical, and (b) ESR spectrum of α-Tocopherxyl radical.

1.7 Measurements and Analyses of Free Radicals and Free-Radical-Induced Oxidation in UHMWPE

1.7.1 Electron Spin Resonance (ESR) Spectroscopy

Electron spin resonance (ESR) or electron paramagnetic resonance (EPR) spectroscopy is a technique for studying materials with one or more unpaired electrons, such as organic and inorganic free radicals. The radicals typically produce an unpaired spin on the molecule from which an electron is removed. The focus of this project is the study of the ESR spectra of free radicals generated as radiation damage from ionizing radiation. Study of the radicals produced by such radiation gives information about the locations and mechanisms of radiation damage. The basic physical concepts of ESR are analogous to those of nuclear magnetic resonance (NMR), but it is electron spins that are excited instead of spins of atomic nuclei. Therefore, this technique finds application in physics, chemistry, biology and, medicine.

The theory behind ESR states that each unpaired electron has magnetic moments associated with its spin. When the molecules of a solid exhibit paramagnetism as a result of unpaired electron spins, transitions can be induced between spin states by applying a magnetic field and then supplying electromagnetic energy, usually in the microwave range of frequencies. The magnetic moments would align either parallel or antiparallel with specific energy in response to the external magnetic field due to the Zeeman Effect. As a result, the energy states of spin up and spin down split, and electronic transition occurs between the states by absorbing the supplied microwave energy [12]. The resulting absorption spectra are described as electron spin resonance (ESR) spectra. More details are provided in Chapter 2.

1.7.2 Thermally Stimulated Luminescence (TSL) Spectroscopy

Luminescence is the emission of light from an object following initial absorption of energy from some a source of energy which could be radiation or thermal energy. Thermally

stimulated luminescence or thermoluminescence is a form of luminescence exhibited by certain crystalline materials, such as some minerals, when previously absorbed energy is re-emitted as light upon heating of the material. Thermoluminescence is a standard technique for radiation dosimetry and archeological dating. It is based on the excitation of an electron in a material which becomes trapped then thermally stimulating the electrons to de-excite to the lowest energy state or equilibrium [13].

Thermoluminescence in polymers is used to study the molecular motion. TSL of polymers involves ionizing radiation production of positive ions (luminescent centers) and trapped electrons. When the temperature is increased, the electrons become de-trapped through the onset of molecular motion, thermal stimulation, or by tunneling through the potential barriers associated with the traps. The de-trapped electron may be re-trapped if other trapping centers exist along its path to the luminescent center. When the electron finally recombines, it induces an excited state of the neutral luminescent center which then emits a photon as it decays to the ground state. The total light output as a function of temperature is called the glow curve which usually exhibits several maxima. TSL is more explained in Chapter 2.

1.8 Literature Review

In 1993, M. S. Jahan has used thermoluminescence (TL) technique, which is simple but fast and sensitive, as a diagnostic tool to test short-term or initial (immediately following sterilization) oxidation of UHMWPE [14].

In 2000, D. W. Cooke et al. have studied X-ray-induced damage in a segmented poly(ester urethane) copolymer, by thermally stimulated luminescence, radioluminescence, optical absorption and electron spin resonance techniques over a wide temperature range [15].

In 2002, M. S. Jahan et al. investigated the effect of post-irradiation storage conditions such as liquid nitrogen (LN), saline solution at 37°C, and a dry atmosphere at RT on thermoluminescence (TL) from ultra-high molecular weight polyethylene (UHMWPE) [16].

In 2007, M. D. Ridley and M. S. Jahan studied vitamin E doped γ-irradiated UHMWPE in nitrogen (N2) or air using ESR technique [17].

In 2008, Ebru Oral et al. proved that high pressure annealing could be used to eliminate the free radicals, formed during irradiation, without a reduction in UHMWPE strength [18].

In 2011, Valentina Brunella and Maria Cristina Paganini employed EPR to detect and characterize a series of different radical species generated in UHMWPE via electron beam irradiation [19].

In 2012, Malik Sajjad Mehmood et al. investigated the effect of high dose of gamma-irradiation on residual radicals' concentration in ultra-high molecular weight polyethylene (UHMWPE) in the presence of vitamin E [20]. M L Chithambo studied thermoluminescence of beta irradiated ultra-high molecular weight polyethylene for measurements between 30 and 200 ◦C and different irradiation time [21].

In 2013, Malik Sajjad Mehmood et al. studied the thermal effects on ultra-high-molecular-weight polyethylene (UHMWPE) residual radicals during the vitamin E diffusion process [22].

In 2014, Malik Sajjad Mehmood et al. diffused vitamin E into the UHMWPE, and investigated the effect of this heat on free radicals [23]. Natalie Hope and Anuj Bellare investigated the effect of various antioxidants on the oxidative stability and crosslink density in HXLPE, for only one value of antioxidant concentration [24].

In 2015, Farzana Ansari et al. concluded that cross-linking improves the wear resistance of UHMWPE but with a compromise in fatigue fracture resistance along with susceptibility to oxidation and fatigue wear in vivo [5].

In 2016, M. S. Jahan et al. did a comparative study of radiation effects in medical-grade polymers: UHMWPE, PCU and PEEK immediately after irradiation in order to study the radiation-sensitivity of these polymers [25]. Leonardo Puppulin et al. found that the lowest value of oxidation index (OI) belongs to non-highly cross-linked polyethylene blended with vitamin E, which were equal to zero in the pristine and also after 28 days of accelerated aging without preliminary irradiation conditioning step [26].

In 2017, Kengo Yamamoto et al investigated the chemical and mechanical properties of vitamin E-doped Highly Cross-Linked PolyEthylene (HXLPE) and proved that the most significant parameters which can greatly affect these properties are vitamin E concentration and cross-link density [27]. Anja Kömmling et al. showed that γ-irradiation led to an increase of the degree of crystallinity and leading to shorter and thus more mobile chains [28].

1.9 Research Objectives

This project is focused mainly on three groups of medical grade UHMWPE samples.

1.9.1 GUR 1050 and GUR 1020 and X-ray Irradiation

The first group of samples includes vitamin E doped samples and non-vitamin E samples, both non-irradiated, which were stored in open air at room temperature (23°C) for more than 10 years. In this group, samples got irradiated with X-ray after 10 years of shelf-storage. Same as group A, this group also has been tested with ESR and TSL spectroscopy.

1.9.2 GUR 1020 and γ-Irradiation

In the second group of samples, vitamin E containing GUR 1020 samples were γ irradiated (30 kGy) more 10 years ago and have been stored in open air at room temperature (23°C). These samples were tested by both ESR and TSL spectrometer.

1.9.3 GUR 1050 and GUR 1020, and Forced Thermal Oxidation

In the last group, non-irradiated samples doped with vitamin E and also non-irradiated non-vitamin E samples were forced to oxidized using thermal oxidation. Then samples were tested with TSL spectrometer.

The ultimate goal of this research project was to determine the long-term effects of vitamin E upon the production of free radicals during sterilization with g-ray and X-ray. In addition, another objective was to determine whether vitamin E had any anti-oxidation effect on the free-radical induced oxidation of sterilized UHMWPE or not. Also, it is worth mentioning that these sterilized UHMWPE had been shelf-stored in a room environment for a long time (more than 10 years).

Chapter 2

ESR and TSL Theory and Technique

2.1 ESR Theory

Orbital electrons have an intrinsic property known as spin. The spin of the electron (m_s) has a value of ½ and is either spin up (+) or spin down (-). Electron pairs in an orbit have opposite spins but the same energy value in absence of an external magnetic field. When in the presence of an external magnetic field, the energy levels for spin up and spin down electrons are no longer degenerate. This splitting is known as Zeeman Effect.

In electron spin resonance, energy level separations are induced with a variable external magnetic field. Perpendicular to the external magnetic field is another magnetic field set at a specific frequency in the microwave range (See Figure 2.1 below).

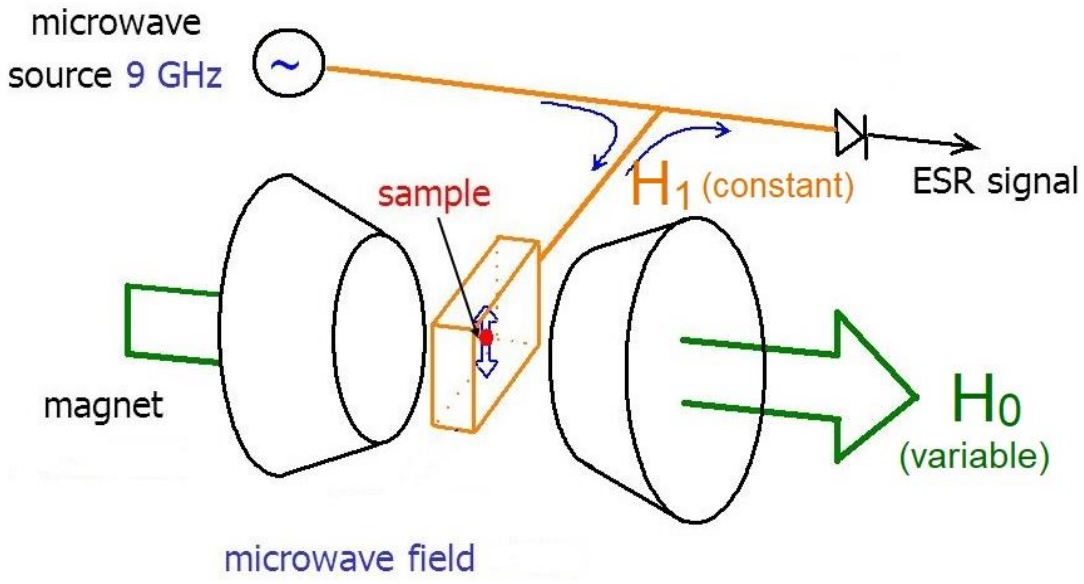


Figure 2.1 ESR diagram.

When the separation of energy levels equals to the energy of the fixed microwave field ($\Delta E = h\nu$), absorption occurs and can be detected by measuring the change in the

detected current in the microwave diode detector. Figure 2.2 below illustrates the energy level diagram.

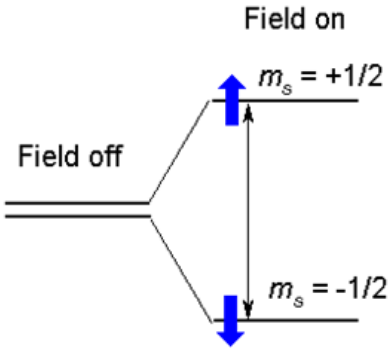


Figure 2.2 Energy level diagram for a free electron in absence and presence of an external magnetic field

The strength of the magnetic dipole is characterized by the dipole moment, μ, which is defined in terms of the interaction of the magnetic dipole moment ($\vec{\mu}$) with an external magnetic field ($\vec{B}$), the energy E of the magnetic moment is given by [12]:

$$E = -\vec{\mu}.\overrightarrow{H_0}$$

$$E = -\mu H_0 \cos\theta$$

$$E = -\mu_z H_0 \quad (1)$$

Where μ is defined as the magnetic moment of an electron and is proportional to the electron spin ($\vec{S}$), and μ_z is the component of μ in the direction of H_0.

$$\vec{\mu} = \frac{g(-e)}{2m_e}\vec{S} \quad (2)$$

or

$$\vec{\mu} = -\frac{g\mu_B}{\hbar}\vec{S} \quad (3)$$

Where g is related to gyromagnetic ratio, m_e is the mass of an electron, and μ_B is called Bohr magneton:

$$\mu_B = \frac{e\hbar}{2m_e} \quad (4)$$

As a result, μ_z will be calculated as below:

$$\mu_z = -g\mu_B M_s \tag{5}$$

Now, E can be written in terms of μ_B and H_0 [12]:

$$E = g\mu_B H_0 M_s \tag{6}$$

Therefore, E is different for the two sorts of spin:

$$E_+ = +\frac{1}{2} g\mu_B H_0 \qquad \text{for} \qquad M_s = +\frac{1}{2} \text{ (spin up)}$$

$$E_- = -\frac{1}{2} g\mu_B H_0 \qquad \text{for} \qquad M_s = -\frac{1}{2} \text{ (spin down)} \tag{7}$$

The difference between two energy states in presence of an external magnetic field ($\overrightarrow{H_0}$) equals to:

$$\Delta E = E_+ - E_- = g\mu_B H_0 \tag{8}$$

When this energy difference is equal to the energy of microwave source ($h\nu$), absorption occurs:

$$h\upsilon = g\mu_B H_0 \tag{9}$$

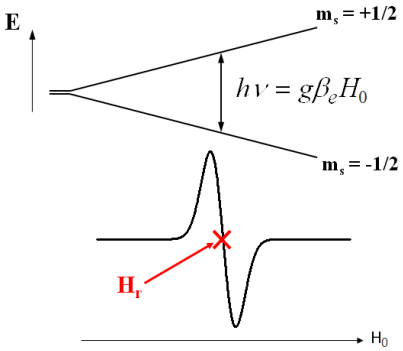


Figure 2.3 Energy level difference leading to absorption (top) and the corresponding ESR spectrum for a free electron (bottom)

2.1.1 *g*-Values

g values are related to the gyromagnetic ratio (γ) commonly reported in NMR studies. $\gamma = \frac{g\mu_B}{\hbar}$, where μ_B is the Bohr Magneton. Free electrons have a g value of 2.00232. g value of a radical species can be used as an identifying factor for free radical spectra. The g value can

be related to the fixed microwave frequency and the magnetic field of resonance with the equation below:

$$g = \frac{h\nu}{\mu_B H_r} \tag{10}$$

H_r is the magnetic field at resonance and ν is the frequency of the ESR spectrometer at the time of the scan [29].

In ESR spectrometer, the magnetic field (in Gauss) varies during scanning and the frequency of microwave source radiation is held constant in (GHz). The energy difference between electronic states is varied as a function of varied magnetic field, when this value matches with frequency of source radiation, transition occurs through absorption of source radiation by unpaired electron.

2.1.2 ESR Spectrometer

Main components of ESR spectrometer and their function are given below:

2.1.2.1 Magnets

The magnets provide a homogeneous field ($\overrightarrow{H_0}$), which can be varied from 0 to 5000 G. The variable magnetic field can be modulated to decrease the noise in an ESR signal, while also decreasing the resolution of the scan. A lower modulation amplitude will increase the amount of noise, but finer structures will be detected.

2.1.2.2 Cavity

The resonant sample cavity acts like a tuned circuit. When a resonance is obtained from the sample, the impedances of the cavity are changed and a signal is reflected to the crystal detector.

2.1.2.3 Detector and Amplifier

The amplifier following the crystal detector amplifies the signal information. The signal phase detector combined with an integrator and a graphic recorder provides a way to

display the ESR signal. By interfacing with a computer, ESR data is recorded and saved on a hard drive for analysis.

2.1.3 ESR spectra

In ESR measurement, the first derivative of absorption line is recorded, because the first derivative exploits minor differences in the absorption curve which results in a characteristic curve for a particular species of analysis. its first derivative.

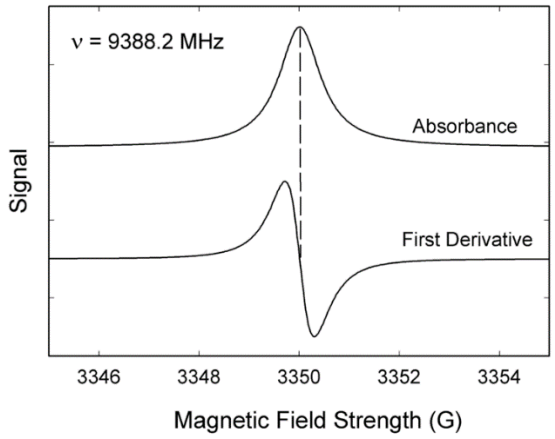


Figure 2.4 ESR absorption signal and its first derivative

The size of the signal is defined as integrated intensity, the area beneath the absorption curve. The integrated intensity is proportional to the number of free radicals. Signal intensity also depends on the value of microwave power. The signal intensity increases with microwave power before it reaches the saturation. When saturation limit is met, increasing the microwave power would yield different results; that is, through increasing the microwave power, the signal diminishes and broadens.

The modulation amplitude is another parameter which affects the intensity of the ESR signal. The intensity of detected ESR signal increases with increased modulation amplitude; however, if the modulation amplitude is too large, the detected ESR signal broadens and becomes distorted.

The ESR spectra are in terms of intensity versus magnetic field. One important factor to analyze a strong ESR spectrum is to measure the peak to peak intensity which is roughly

proportional to the number of radicals. But, for accurate measurement of number of radicals, the first derivative spectra are integrated twice with baseline correction.

2.2 Thermally Simulated Luminescence (TSL) Theory

Luminescence phenomena in solids, like florescence, phosphorescence and TSL have been studied for many years. Luminescence is the emission of light from an object following initial absorption of energy from some form of radiation. The emission is deemed florescence if the characteristic lifetime τ between absorption and emission is such that, $\tau \leq 10^{-8}$ s, and phosphorescence is characterized with τ greater than a few seconds [13].

Thermoluminescence in solids is the light emission (mainly visible) that takes place during the heating of a solid following an earlier absorption of energy from radiation. It is in fact the release, in the form of light, of previously absorbed energy and is quite different from incandescence light emission from a substance that is heated at high temperatures. Once thermoluminescence emission has been observed, the material will not show it again after simply cooling the material and reheating it but has to be exposed to radiation to obtain TL again [30]. It is based on the excitation of electron in a material which becomes trapped then thermally stimulating the electrons to de-excite to the lowest energy state or equilibrium. Once charge carries are initially created, they may remain stable for many years before thermal de- excitation [31]. TSL involves two steps. First, a sample must be exposed to ionizing radiation, then the sample must be heated, which yields light emission, collected by a photomultiplier tube (PMT) and current amplifier. Total light output as a function of temperature is called the glow curve, which usually exhibits several maxima. A typical glow curve containing single maximum temperature (T_m) is shown in Figure 2.5.

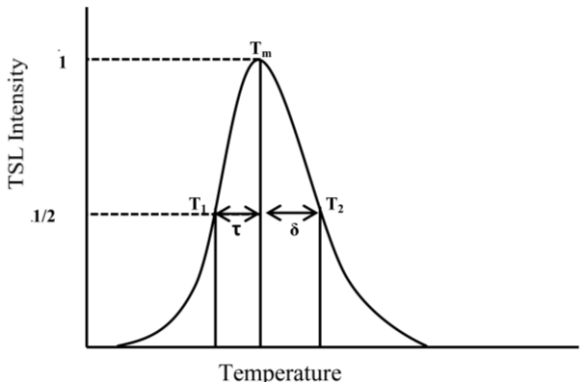


Figure 2.5 A typical TSL glow curve.

The shape of glow curve also depends on the rate of heating. In the figure, the symbols τ and δ represent low and high temperature half width half maximum (HWHM). The temperature T_1, T_2, and T_m are the lower and upper temperatures corresponding to half peak intensity and peak temperature, respectively.

$$\tau = T_m - T_1 \tag{11}$$

$$\delta = T_2 - T_m \tag{12}$$

A block diagram of a TSL spectrometer is shown in figure 2.6.

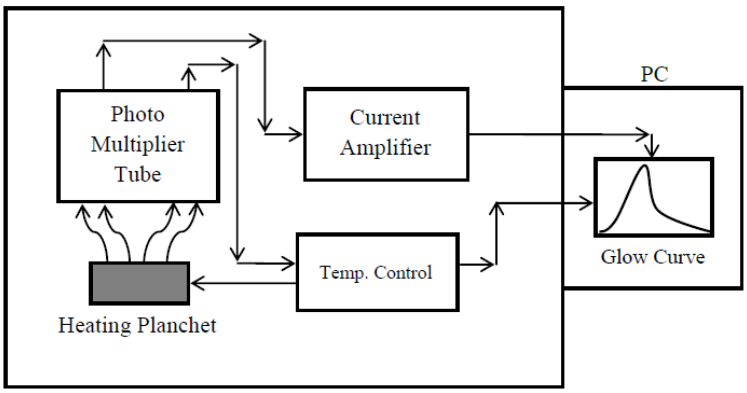


Figure 2.6 A block diagram of TSL spectrometer.

Radiation induced defects in the lattice structure and impurities in the crystal can be grouped into three possible categories:

- Electronic defects which involve changes in valance states,
- Ionic defects which consist of displaced lattice ions,
- Gross imperfection which include voids and dislocation loops [32].

The valance states impurities and the lattice ions can be altered in electronic defects. Valance electrons and holes of the lattice and impurity atoms are first excited by the incident radiation. The electrons are excited to the conduction band and the holes the valance gap. The electrons decay and will be trapped before they can recombine with the holes. The impurities act as traps for the electrons and holes. Also, imperfections in the crystal can act as traps. The most important effect in ionic defects is attributed to the vacancies created by the moving ions. These vacancies contribute more to radiation damage than any other means. Ionic defects involve a two-step process. First, some energy is needed to break a number of bonds, then a smaller number of bonds are reestablished to account for the energy made available, roughly 1 eV [33]. Figure 2.6 is an energy band diagram with details about the electron-hole absorption and emission process.

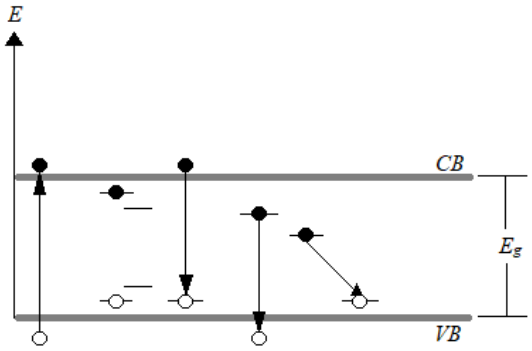


Figure 2.7 Absorption and emission process in solids.

Glow curve characteristics are dependent on the form of radiation used for excitation as well as the dose, but it's possible to reach saturation for high doses. Also, glow curve shape depends on the rate of heating [13].

The probability per unit time of release of an electron from the trap is assumed to be described by the Arrhenius equation

$$p = s\left\{exp\left(-\frac{E_t}{k_B T}\right)\right\} \tag{13}$$

Where, s is frequency factor or attempt-to-escape factor, E_t is trap activation energy, k_B is Boltzmann's constant and T is absolute temperature at which electron is stimulated to escape the trap [13].

2.2.1 TSL in Polymers

TSL was first reported in 1955 and was later used to study molecular motion ant structural transitions. Usually conducted at low temperature (77K), TSL of polymers involve ionizing radiation production of positive ions (luminescence centers) and trapped electrons [34]. When heated, the electrons become de-trapped through the onset of molecular motion, thermal simulation, or by tunneling through the potential barriers associated with the traps. The de-trapped electron may be retrapped if other traps exist along its path to the luminescence center. When the electron finally recombines, it includes an excited state of the neutral luminescence center which then emits a photon as it decays to the ground state [39].

2.2.2 Electron Traps and Luminescence Centers

Four types of traps are considered to exist in polymers: cavity traps, neutral molecules with positive electron affinity, free radicals, and crystalline region defects. Cavity traps are voids between lamellae in the amorphous regions of the polymer which release trapped electrons due to molecular motion [35]. Neutral molecules have been shown to affect the glow curve shape when present in sample. Neutral molecules with positive electron affinities can act as electron traps if sufficient in concentration [36,37]. Free radicals capture electrons and radicals have also been shown to be luminescence centers in PMMA [38]. Traps in crystalline region can be vacancies or chain ends; electrons can escape from these defects by absorption of energy. Traps in crystalline region can also release electrons by molecular motion if the polymer was heated to a sufficient temperature for the crystal to melt [36]. While luminescence is possibly due to impurities within the polymer, electron trapping

results mainly from the basic polymer structure, including radiation induced species and chemical defects [37].

The positive ions remaining after radiation and the excitation of electrons are considered to be luminescence centers if upon electron recombination the positive ions emit photons. The recombination results in an excited state of the luminescence center which de-excites through a radiative transition. Any molecule that readily ionizes without dissociation may be a luminescence center in polymers. Luminescence centers may be direct constituents of the polymer or neutral impurity molecules in the polymer at the time of irradiation [37,39].

2.2.3 TSL in Polyethylene

The general mechanism for TSL in polyethylene is the ionization of luminescence centers followed by the trapping of the electrons. Subsequent heating frees the trapped electrons which then recombine with the luminescence centers including an excited state. The excited states relax to the ground state by emitting a photon [40]. Early TSL studies of Polyethylene have shown the presence of three glow peaks. Glow peaks with differing maximum peak temperature, in which each peak will have different activation energies. These peaks are indicative of the presence of different types of traps, or there may be different types of luminescence centers [37].

Chapter 3

Materials and Methods

3.1 Materials

For the purpose of this project, two grades of UHMWPE (GUR 1020 and GUR 1050) were used to be tested with ESR and TSL spectrometer. Non-vitamin E samples and vitamin E containing samples were irradiated with either X-ray or γ-ray for sterilization. The availability of X-ray source in the Biomaterials Research Lab made it possible to study the immediate effects of irradiation on the behavior of free radicals.

3.1.1 GUR 1050 and GUR 1020, and X-ray Irradiation

The 10-years old shelf stored non-irradiated UHMWPE samples doped with vitamin E were in this group. Vitamin E containing samples were prepared using GUR 1020 resin powder (provided by Ticona) and vitamin E (α-Tocopherol) with 95% purity (provided by Sigma Aldrich). Vitamin E was consolidated with GUR 1020 at different concentration levels (0%, 0.5%, 1%, and 15%). The samples in this group contained different concentrations of vitamin E (0%, 0.5%, 1%, and 15%). All the samples, including vitamin E containing samples and non-vitamin E samples, were irradiated by X-ray (in air at room temperature) followed by 10 years of shelf storage. The X-ray source was set to 50 kV and 40 mA.

The sample tubes for ESR spectroscopy (3.5 mm id x 4.0 mm od, and 200 mm in length) were made out of suprasil quartz (Wilmad Glass). The ESR and TSL spectra of each sample were recorded 3 time and then averaged. The samples, 10 mm in length and 3 mm in diameter (for ESR), were machined from ram extruded rod. For TSL spectroscopy, samples of size 3.8 mm (length) × 2.8 mm (width) × 0.4 mm (thickness) and of mass 4.2 mg to 4.6 mg were tested.

3.1.2 GUR 1020, and γ-Irradiation

The samples of this group were made and irradiated with γ-ray (30 kGy at room temperature) more than 10 years ago. After γ-irradiation, samples were shelf stored (in air at room temperaure) for more than 10 years.

Samples were tested with both ESR and TSL spectrometer. Samples were cut in the same size as the previous group, to keep the consistency for the results comparison.

3.1.3 GUR 1050 and GUR 1020, and Forced Thermal Oxidation

In this group, non-irradiated samples of both vitamin E containing (0.5%, 1%, and 15%) and non-vitamin E UHMWPE were used. Non-irradiated samples forced to oxidize using thermal oxidation. The thermal oxidation process took place in an oven at 160°C for 1 hour in air. After that, samples were tested by TSL spectrometer immediately, 30 minutes, 1 hour, 2 hours, 4 hours, 8hours, 16 hours, 24 hours, 1 day, 2 days, 1 week, 2 weeks, and 1 month after cooldown. Samples were in the same size as in Group A and Group B.

3.2 Methods

Two methods were adopted to study the effects of vitamin E on the free radicals and oxidation behavior of 10 years old UHMWPE samples. Each test, in ESR and TSL technique, was repeated at least three times to get the average result within the experimental error.

3.2.1 ESR Spectroscopy

Electron Spin Resonance (ESR) technique was one of the methods used to analyzed the free radical activities in all the samples using an X-band Varian E-4 spectrometer operating at 9.6 GHz microwave frequency and 100 kHz magnetic field modulation frequency. The samples were tested over 200 Gauss sweep width keeping the constant center magnetic field at 3510 Gauss, which provided 1024 data point in ESR spectra. Samples were placed in a suprasil quartz sample holder which does not create any additional signal in ESR

spectra. The power and modulation amplitude were varied to generate cleaned signal and to detect the different types of free radicals. Figure 3.1 shows the ESR spectrometer which was used in this project.

Figure 3.1 Varian E-4 ESR Spectrometer

The ESR spectra were analyzed using “SigmaPlot” software. All the simulation presented were carried out using WinSim2000. The parameters obtained can be used to determine radical species abundances in ESR spectra, and also help to determine if other overlapping radicals are present in ESR spectra. Spectral simulations were used to study UHMWPE radical morphology in more quantitative way.

3.2.2 TSL Spectroscopy

The UHMWPE films having thickness of 0.4 mm were cut into 3.8 mm × 2.8 mm sample pieces each of masses 4.2 mg to 4.6 mg. The samples were placed in TSL pans (DSC pan without top) for testing. TSL measurements were carried out using a commercial dosimeter, Harshaw QS 3500 (see Figure 3.2), in which heating chamber was continuously purged with dry and filtered Nitrogen gas (N2) to avoid the production of thermally oxidized radicals and moisture.

Figure 3.2 Harshaw QS 3500 TSL Spectrometer

The samples were heated from 40°C to 400°C at a rate of 1 /s. The resulting TSL intensity (glow curve) was recorded as a function of temperature using WinREMS software interface. Each of the glow curves were then deconvoluted into an individual glow peaks using peak-fit software. The glow peak parameters of the individual peaks were then calculated using curve fitting software PeakFit V4.

Chapter 4

Results and Discussion

In the present study, three specimens were tested for each type of sample and the average result was taken for analysis.

The entire experimental results took place using two different methods for three groups of samples mentioned in Chapter 3. In one method, the results are presented using ESR spectra (line graphs) which indicate the intensity of free radicals. The structure of ESR spectra also is an indication of the presence of different types of radicals. Another method (TSL) records the glow curve intensity in arbitrary units as a function of temperature. Each glow curve was analyzed using a curve fitting software to obtain glow curve parameter.

4.1 Results of GUR 1050 and GUR 1020, and X-ray Irradiation

GUR 1050 (non-vitamin E) and GUR 1020 (vitamin E containing) samples followed by 10 years of aging in air at room temperatures (23°C) were X-ray irradiated and brought under ESR and TSL spectrometry and analysis. In this study, the behavior of free radicals was investigated in samples with different concentrations of vitamin E. All the samples were irradiated using X-ray.

ESR spectra, resulting from free radical detection, were present in all samples (with or without vitamin E). Each spectrum was a superposition of different kinds of free radicals; mostly allyl, alkyl, and polyenyl. There was also observed a change in position of peaks as a function of time, indicative of reactions of the radicals with oxygen, and therefore probable oxidation.

In a set of experiment, samples with different concentrations of vitamin E were X-ray irradiated for 5 minutes and tested with ESR spectrometer immediately, 5 hours and 24 hours after irradiation. The results can be seen in Figures 4.1-4.3.

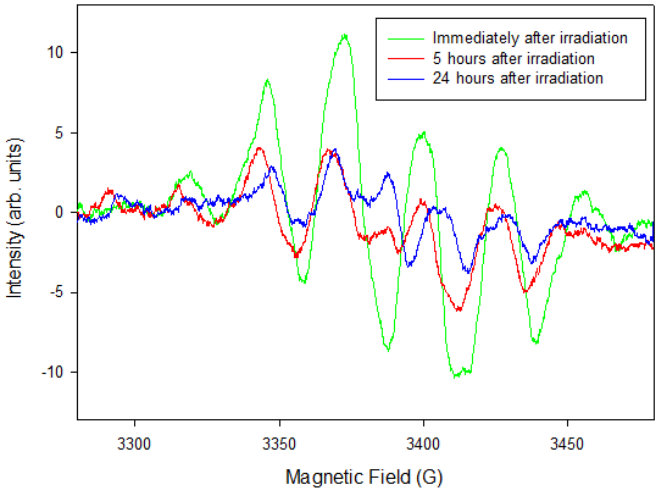


Figure 4.1 GUR1020 sample containing 15% vitamin E, X-ray irradiated for 5 min.

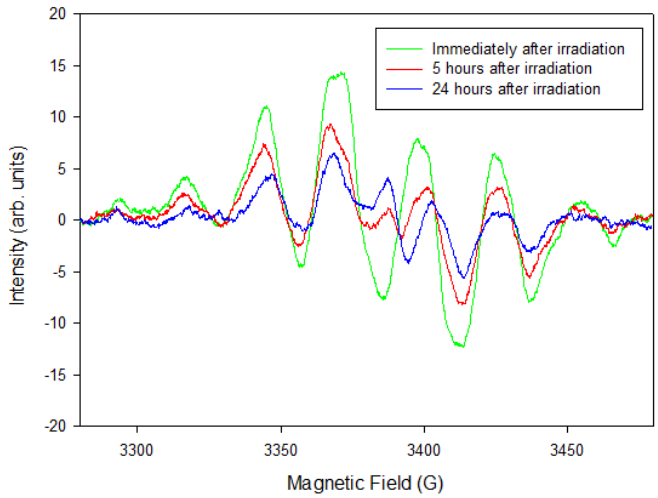


Figure 4.2 GUR1020 sample containing 1% vitamin E, X-ray irradiated for 5 min.

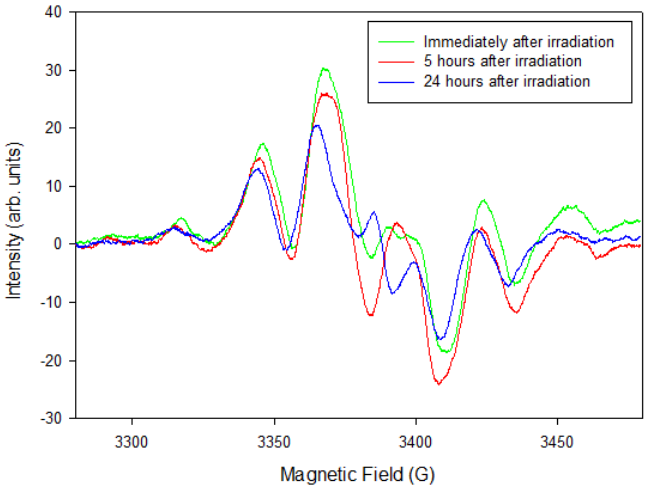


Figure 4.3 GUR1050 sample without vitamin E, X-ray irradiated for 5 min.

Each spectrum is a composition of different types of free radicals. A comparison of simulated signals and experimental signals of samples with different concentrations of vitamin E, immediately after irradiation, is illustrated in Figure 4.4.

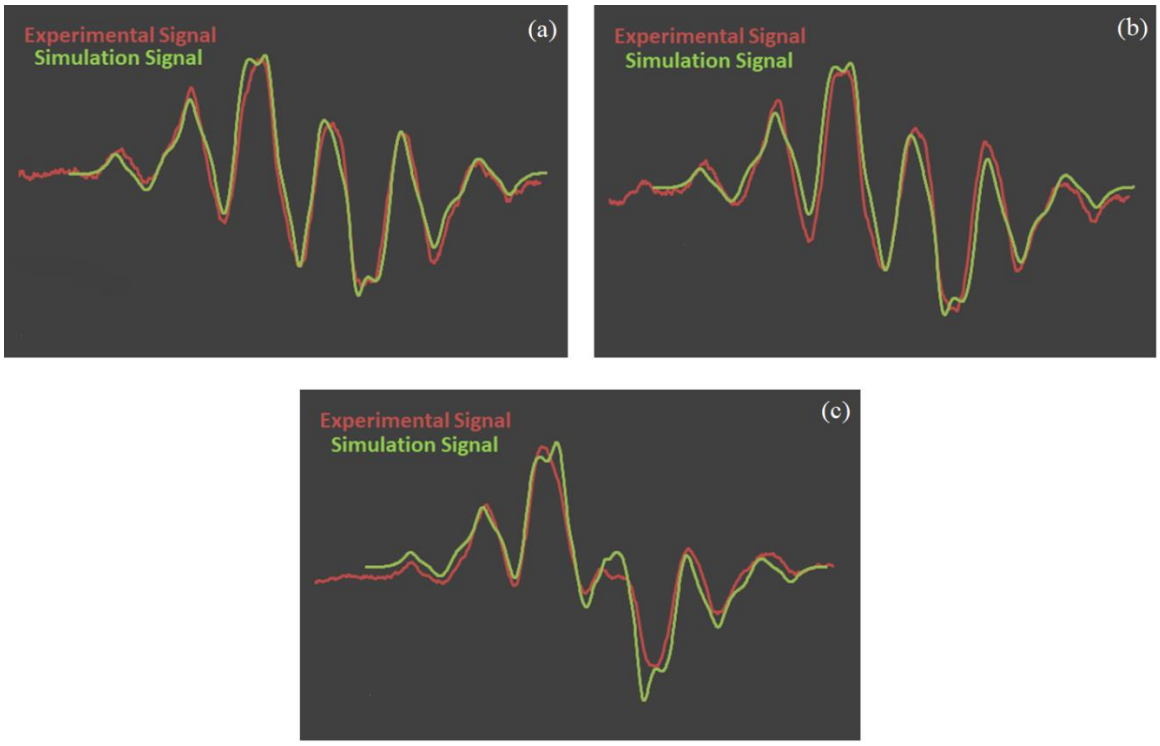


Figure 4.4 Simulated and experimental ESR signals of X-ray irradiated UHMWPE for 5 min, immediately after irradiation, with (a) 15%, (b) 1%, and (c) 0% Vitamin E.

In all the graphs, the growth of a singlet in the center of the spectrum can be seen. Although the small singlet at the center of the spectrum is in the region of the Vitamin E signal, it is not from Vitamin E, since it can be seen in non-vitamin E samples as well. It is most likely from Oxygen-Induced Radicals (OIR), polyenyl, or oxygen-centered polyenyl [41]. Our simulation tool did not have OIR types of radicals available as "ingredients" at the time of this writing, so cannot fully match the experimental spectra which contain OIR. Immediately after irradiation, the experimental signal is able to be simulated better, because there has been less opportunity for oxidation, and therefore less OIR-type of free radicals present. In Figure 4.5 simulated and experimental signals of samples with 1% vitamin E are shown. The central singlet is indicated by the yellow arrow. The growth of the central peak is a result of decay of other species caused by oxidation process, which is caused by storing in air. As time goes on, the intensity of this peak increases. Another parameter that affects the intensity of this peak is the microwave power. Based on previous studies, if the samples were stored in an inert environment, this behavior would not be observed [42].

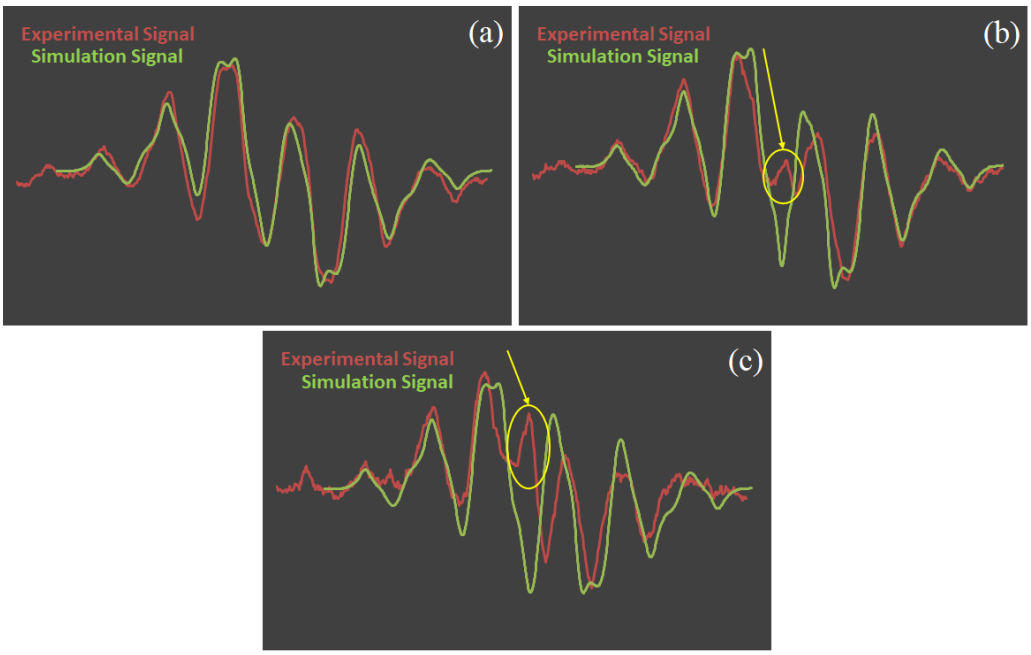


Figure 4.5 Simulated and experimental ESR signals of GUR 1020 containing 1% vitamin E (a) immediately, (b) 5 hours, and (c) 24 hours after irradiation

Figure 4.6 indicates the peak-to-peak height of the central singlet, in different vitamin E concentrations, as the time passes. An observable fact from this graph is that the central singlet in vitamin E containing samples appears 5 hours after irradiation, but for non-vitamin E samples, this peak appears 24 hours after irradiation. By the way, the intensity of this singlet in vitamin E containing samples is not as high as the one in non-vitamin E samples. It can be concluded that the oxidation rate in vitamin E containing samples is lower than that in non-vitamin E samples.

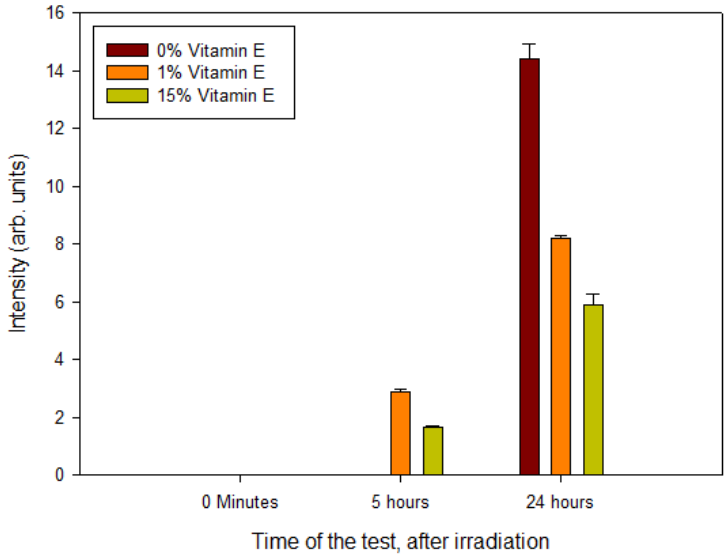


Figure 4.6 Peak-to-peak height of the central singlet

Table 4 represents a comparative composition of different type radicals within the GUR 1020 and GUR 1050 samples stored in air at room temperature. The analysis shows that after irradiation, vitamin E free radicals can be detected from ESR spectra. Even though the percentage of existing free radicals a very small, their presence implies that, after even 10 years, vitamin E still is active inside the polymer. This analysis was performed using an in-house-created software program.

Table 4 - Free Radical types detected in UHMWPE samples with different concentration of vitamin E

Types of Radicals	GUR 1020 (with 15% vitamin E)	GUR 1020 (with 1% vitamin E)	GUR 1050 (without vitamin E)
Alkyl	81%	74%	54%
Allyl	7%	8%	19%
Polyenyl	6%	14%	15%
Dienyl	-	3.3%	15%
Trienyl	-	-	-
Vitamin E	6%	0.7%	-

It can be concluded from the table that as the concentration of vitamin E increases the number of Alkyl radicals increases as well. The number of Allyl radicals is noticeably higher in non-vitamin E samples compared to vitamin E containing samples. Dienyl radicals cannot be detected when the concentration of vitamin E is relatively high (15%).

The effect of the irradiation exposure on different concentrations of vitamin E can be seen in Figures 4.7-4.9.

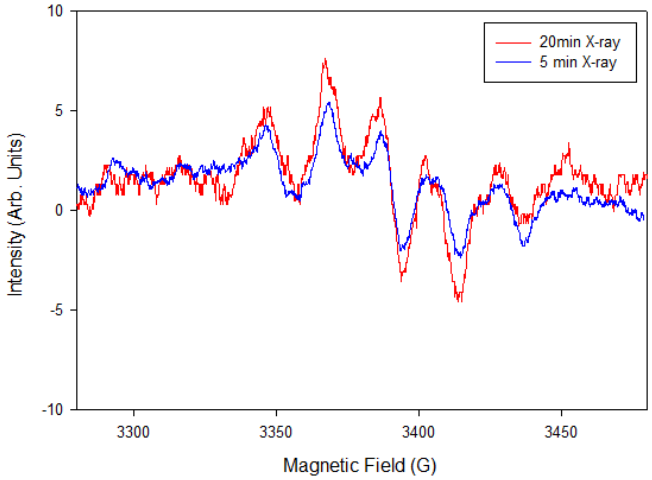


Figure 4.7 Effect of X-ray irradiation time on the sample containing 15% vitamin E

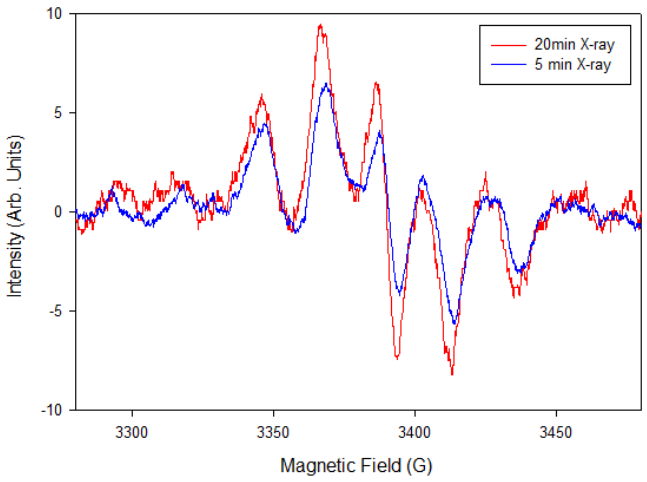


Figure 4.8 Effect of X-ray irradiation time on the sample containing 1% vitamin E

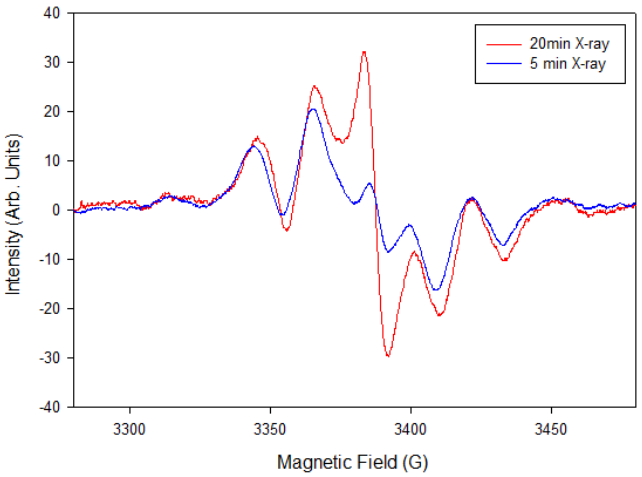


Figure 4.9 Effect of X-ray irradiation time on the sample containing 0% vitamin E

As it was expected, the graphs indicate that the intensity of different species of free radicals increases as the duration of irradiation increases.

Along with the ESR spectroscopy, TSL was also performed on the X-ray irradiated samples with different concentration of vitamin E to complete the investigation of the free radicals behavior. Figures 4.9-4.11 show the difference in TSL glow curve of irradiated and non-irradiated samples with different vitamin E concentration. Figures 4.10-4.13 shows glow peaks of X-ray irradiated vitamin E containing samples and non-vitamin E samples.

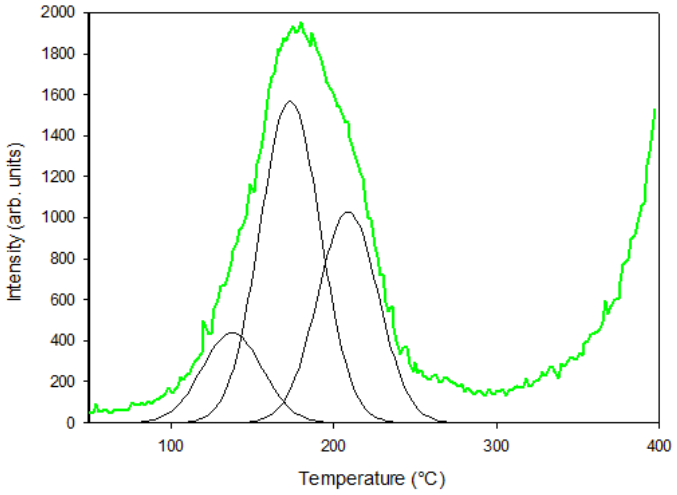


Figure 4.10 Glow peak of X-ray irradiated 15% vitamin E containing GUR 1020

X-ray irradiated GUR 1020 with 15% vitamin E produces three peaks in luminescence measurements at approximately 130°C, 175°C, and 210°C. The low temperature peak was previously attributed to the melting of the crystallites in low-density polyethylene (LDPE), but in UHMWPE the crystallites do not melt below 130°C [2,43]. The high temperature peak (210°C) is ascribed to the decomposition of peroxides [43].

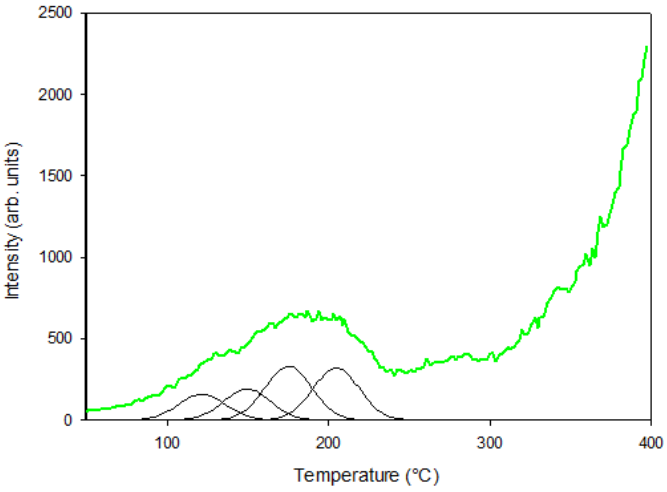


Figure 4.11 Glow peak of X-ray irradiated 1% vitamin E containing GUR 1020

Four peaks were observed near 125°C, 150°C, 175°, and 210°C after TSL analysis of X-ray irradiated GUR 1020 with 1% vitamin E. The high-temperature and low-temperature peaks are almost the same as those for 15% vitamin E containing samples.

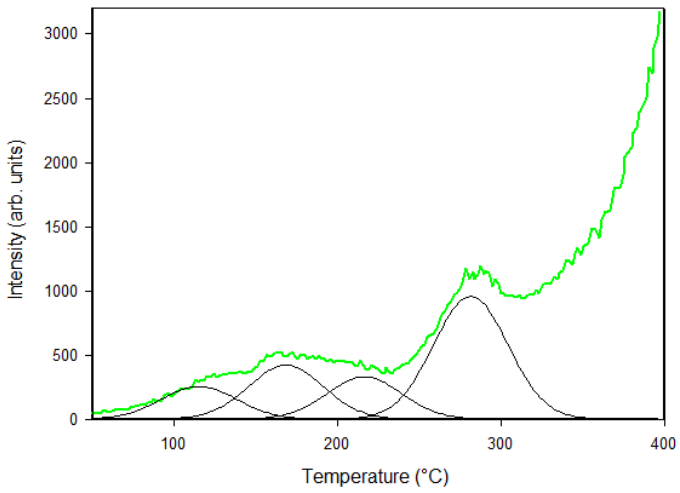


Figure 4.12 Glow peak of X-ray irradiated 0.5% vitamin E containing GUR 1020

The three out of four luminescence peaks for X-ray irradiated GUR 1020 with 0.5% vitamin E are the same as those for 15% and 1% vitamin E containing samples. One additional peak is observed at 280°C.

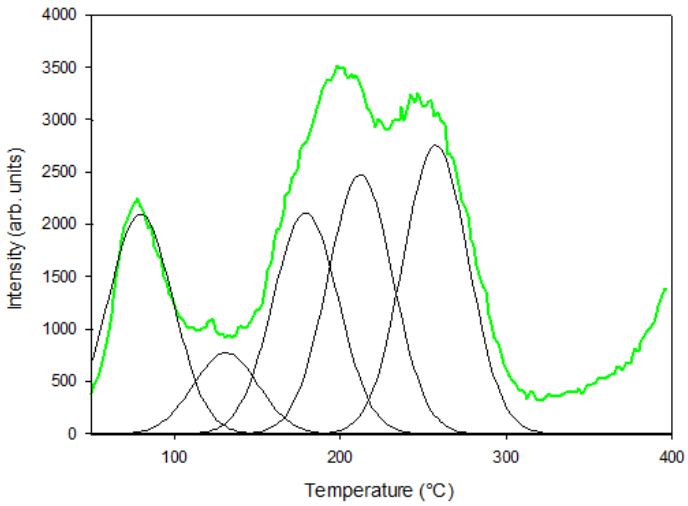


Figure 4.13 Glow peak of X-ray irradiated GUR 1050 (non-vitamin E)

Besides the common peaks around 130°C, 175°C, and 210°C, two more peaks were observed for X-ray irradiated non-vitamin E containing samples. One around 80°C and the other one around 260°C. The last-mentioned peak (at 260°C) might be from the same species as the 280°C peak in 0.5% vitamin E containing samples, which disappears for higher concentrations of vitamin E.

All the previous graphs were recorded immediately after 5 minutes of X-ray irradiation. In order to investigate the behavior of the glow curve as a function of time passed after irradiation, the recording was continued up to three days after irradiation for vitamin E containing samples. The analyzed glow curves of X-ray irradiated GUR 1020 containing 15% vitamin E are illustrated in Figure 4.14. Sample was X-ray irradiated for 5 minutes.

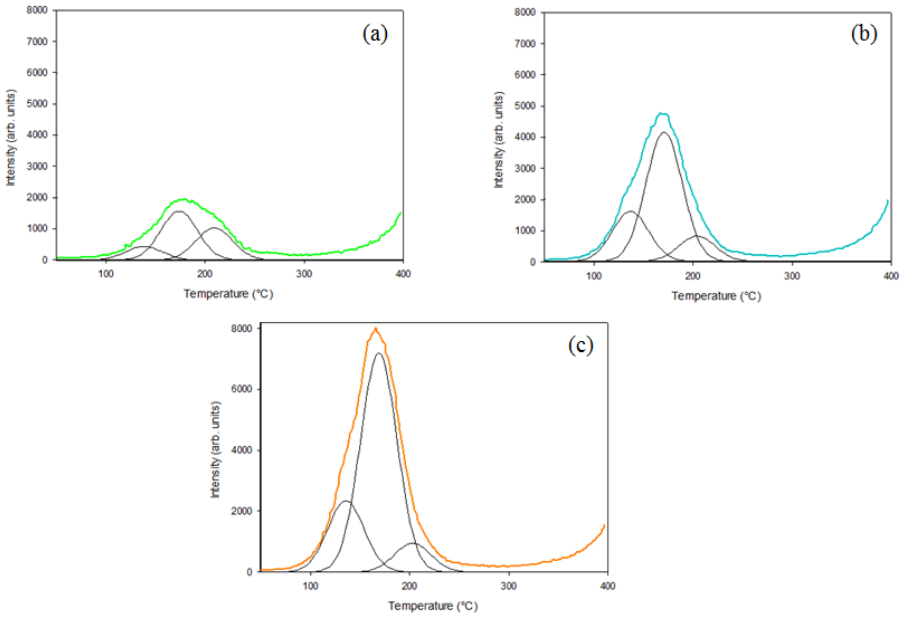


Figure 4.14 Peak analysis of X-ray irradiated GUR 1020 with 15% vitamin E, (a) immediately, (b) 24 hours, and (c) 3 days after irradiation.

It can be seen from the graphs that as time passes no shift in peaks occurs for 15% vitamin E samples. However, this behavior changes as the concentration of vitamin E decreases. For samples with 1% vitamin E, peaks slightly are sifted toward the higher temperature values. After three days, a new peak seems to have appeared at 280°C. For samples with 0.5% vitamin E, the same as 1% vitamin E samples, a shift towards the higher temperature is observed and eventually after 3 days, a new peak at 310°C appears.

Figures 4.15-1.17 show the details about time-dependent trend of the intensity and location of the glow curves.

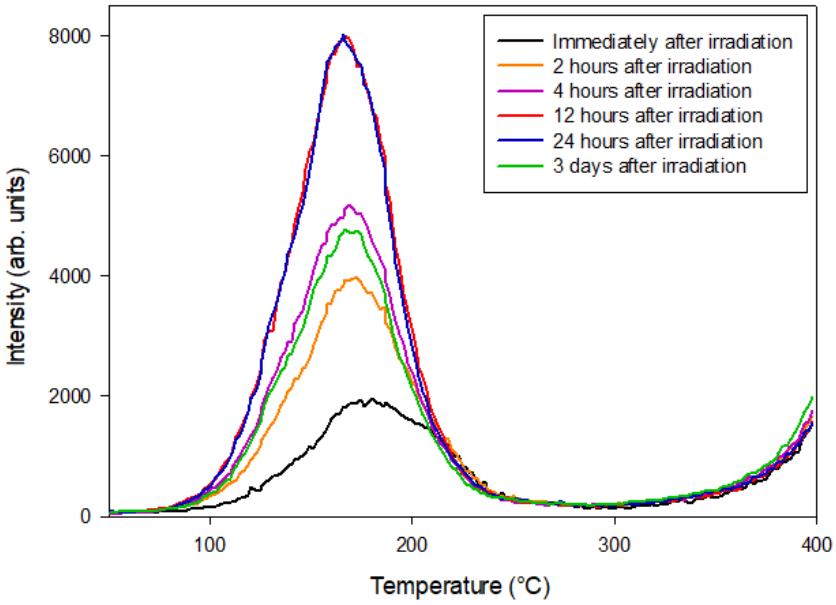


Figure 4.15 Glow curves of 15% vitamin E containing GUR 1020, X-ray irradiated for 5 minutes.

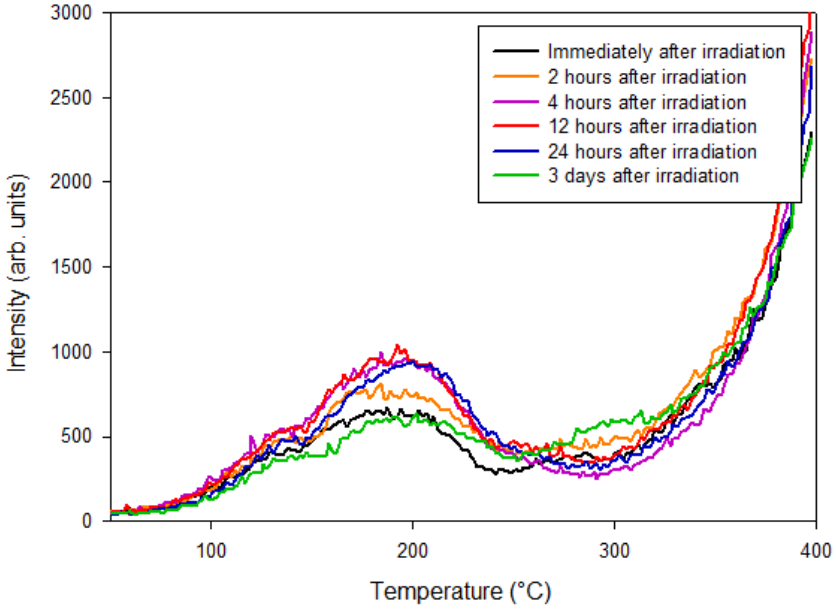


Figure 4.16 Glow curves of 1% vitamin E containing GUR 1020, X-ray irradiated for 5 minutes.

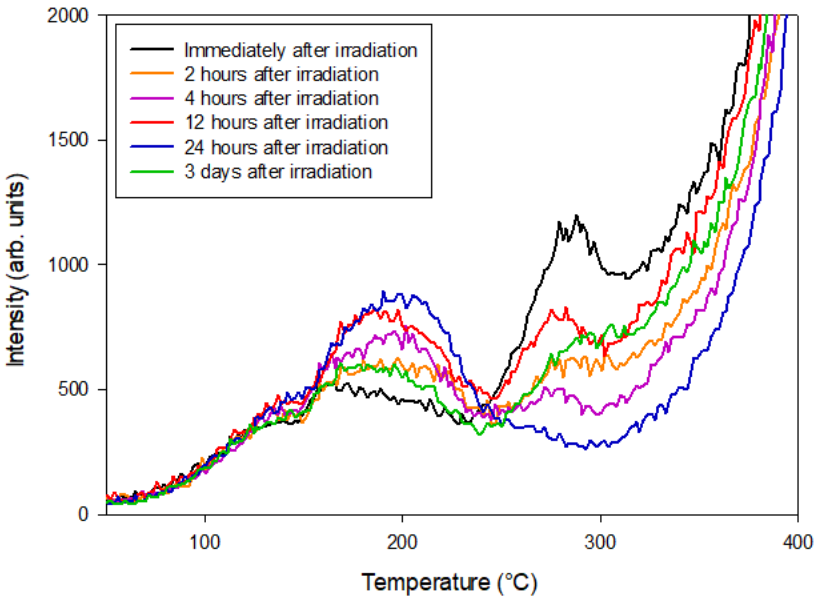


Figure 4.17 Glow curves of 0.5% vitamin E containing GUR 1020, X-ray irradiated for 5 minutes.

The same trend can be observed in all the graphs for each concentration of vitamin E. The intensity of the glow curves increases until 24 hours after irradiation and decreases afterwards. However, the decreased value of the intensity (three days after irradiation) is not lower than the initial (immediately after irradiation) intensity of the glow curve. In addition, a slight shift in T_{max} occurs, for low concentrations of vitamin E, as the time passes. This is a result of oxidation since the samples rest in air. The similar behavior of the intensity of the glow curve as a function of time, for different concentrations of vitamin E, is shown in Figure 4.18.

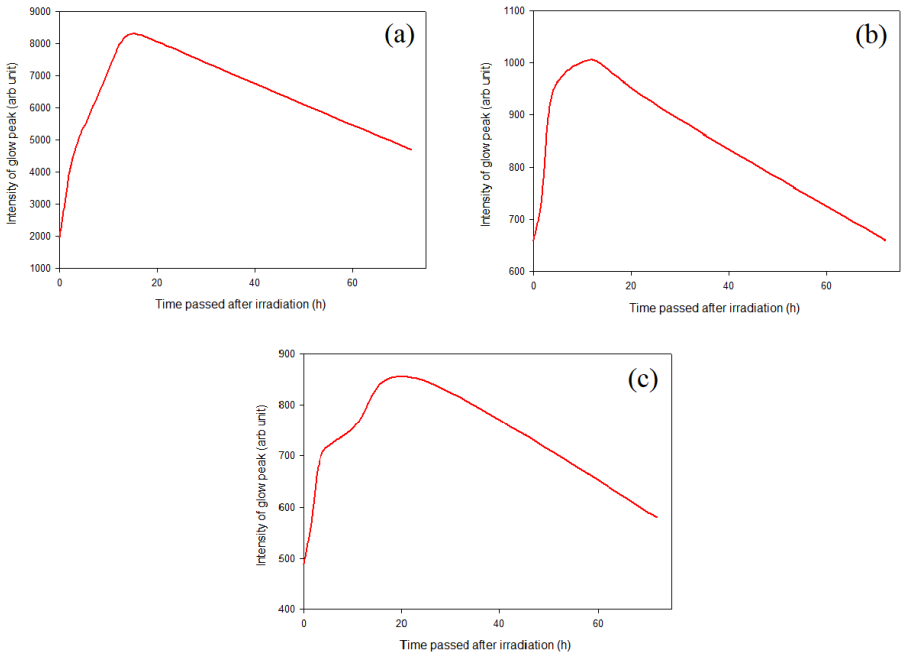


Figure 4.18 Behavior of the intensity of the glow peak as a function of time for GUR 1020 containing (a) 15%, (b) 1%, and (c) 0.5% vitamin E.

The same behavior is observed for non-vitamin E samples, except the fact that in this case the shape of the spectrum changes after irradiation (see Figure 4.18). In terms of analysis, the spectra of irradiated and non-irradiated samples were compared. For vitamin E containing samples, no detectable difference has been found between non-irradiated and X-ray irradiated samples, except a decrease in the intensity of the glow peak, which has been observed for all the vitamin E concentrations. However, for non-vitamin E samples, a change in the shape of the glow curve was observed after irradiation (Figure 4.19). As can be seen from the graph, a high intensity peak appears after irradiation, which does not appear for vitamin E containing samples.

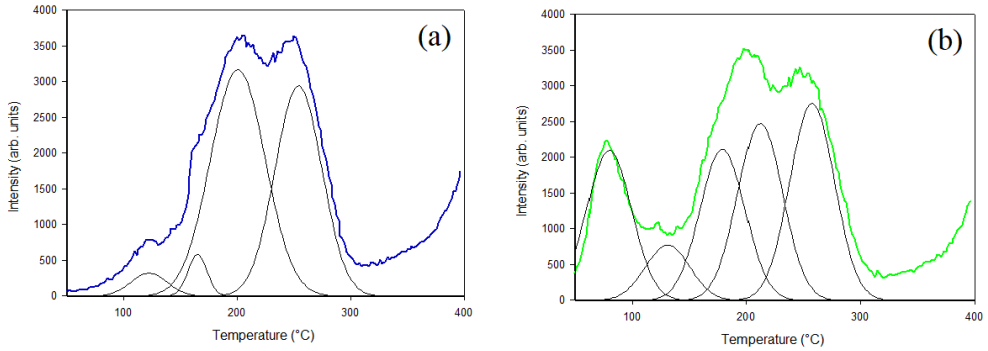


Figure 4.19 A comparison between TSL spectra of (a) non-irradiated and (b) X-ray irradiated (5 minutes) GUR 1050 without vitamin E.

Figure 4.20 represents comparative graphs of irradiate and non-irradiated spectra if vitamin E containing GUR 1020. The fact that any additional peak, after irradiation, has not been detected only in vitamin E containing samples might be a result of the presence of vitamin E.

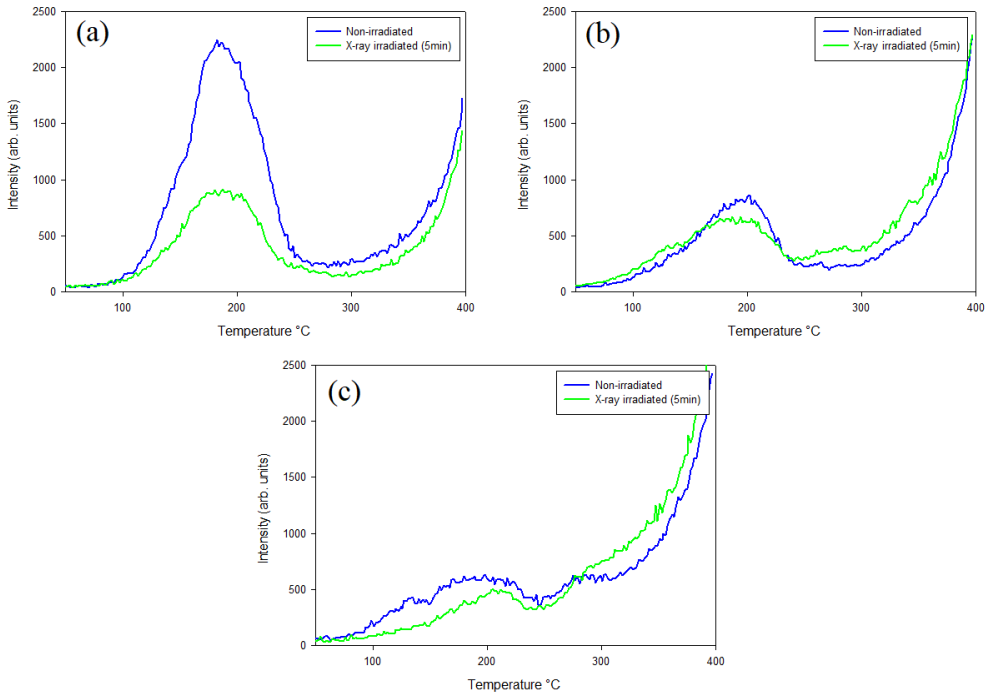


Figure 4.20 A comparison between TSL spectra of non-irradiated and X-ray irradiated (5 minutes) GUR 1020 containing (a) 15%, (b) 1%, and (c) 0.5% vitamin E.

4.2 Results of GUR 1020, and γ-Irradiation

GUR 1020 (vitamin E containing) samples were irradiated by γ-ray and stored in air at room temperatures (23°C) for more than 10 years. Samples, as in previous section, were tested using two different methods: ESR and TSL.

The γ-irradiated GUR 1020 samples with different concentrations of vitamin E shelf stored in air and at room temperature (23°C) were brought under analysis. Many reports have been published stating that thermal annealing increases the oxidative stability of the polymer [A40-42]. However, a considerable number of free radicals in GUR 1050 samples have been observed even after 10 years of shelf-storage. Figure 4.21 compares the amount of free radicals in γ-irradiated and n0n-irradiated samples for different concentrations of vitamin E.

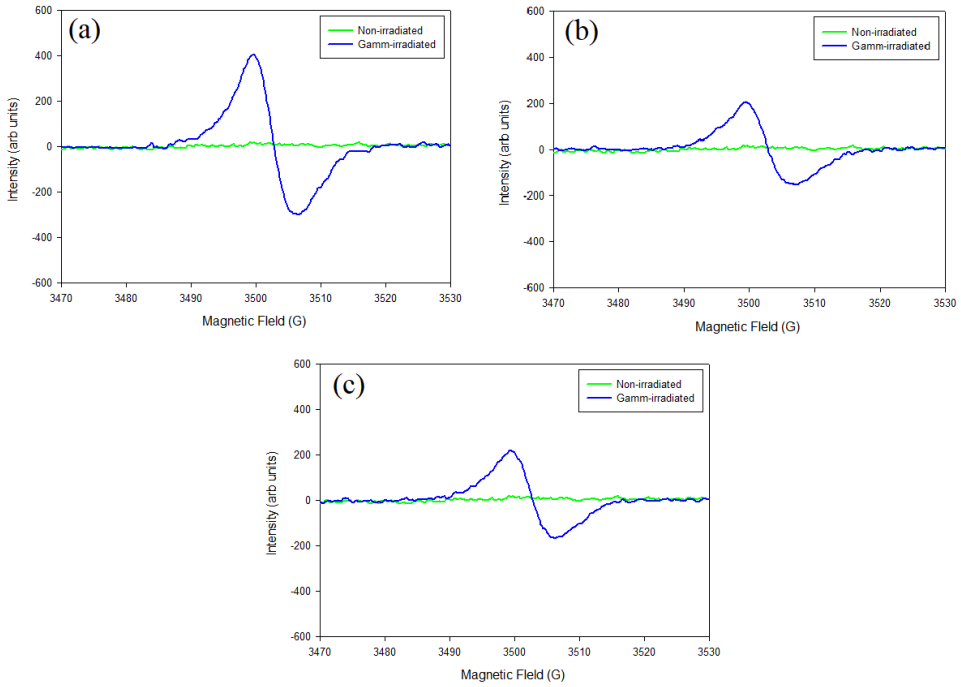


Figure 4.21 Comparative ESR spectra of γ-irradiated and non-irradiated GUR 1020 samples containing (a) 15%, (b) 1%, and (c) 0.5% vitamin E.

ESR spectra recorded in the present study (10 years after irradiation) indicate the presence of oxygen-induced polyenyle radicals in samples aged at 23°C in open air. This

result shows that, at room temperature most of the primary radicals of GUR 1050 have been converted to the oxygen induced radicals in presence of air.

TSL spectroscopy was performed for this set of samples, as well. Peak analysis for the glow curve of γ-irradiated GUR 1020 with different concentrations of vitamin E has been done and the result is shown in Figure 4.22.

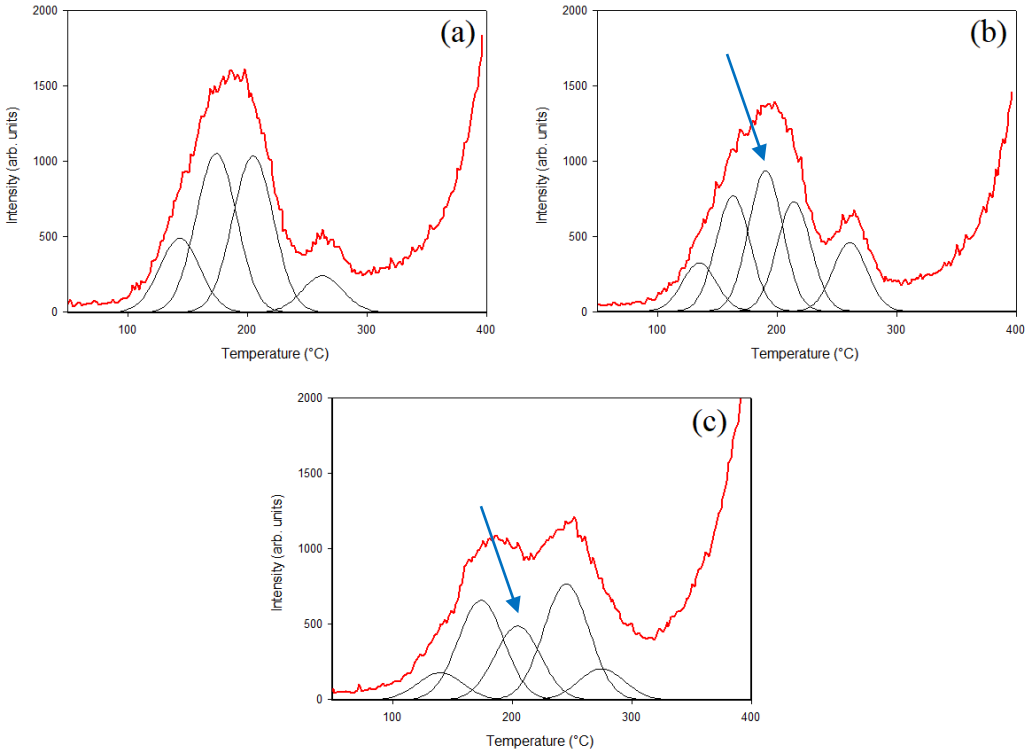


Figure 4.22 Peak analysis for the glow curve of γ-irradiated GUR 1020 with (a) 15%, (b) 1%, and (c) 0.5% vitamin E

There are four peaks which are present in all three spectra. Three out of these four peaks are the same as those for X-ray irradiated samples; and one additional peak around 260°C. Besides these four peaks, another peak (around 200°C) is observed for samples with 1% and 0.5% vitamin E, which could be assigned to the concentration of vitamin E since it's not detectable for higher percentage of vitamin E. This peak is indicated by blue arrows in Figure 4.22.

4.3 Results of GUR 1050 and GUR 1020, and Forced Thermal Oxidation

GUR 1050 (non-vitamin E) and GUR 1020 (vitamin E containing) 10-year old samples were forced to thermal oxidation in air at 160°C for 1 hour. Samples were tested immediately after cooldown up to one month after cooldown.

To investigate the effects of thermal oxidation, a comparative TSL spectra of control samples and thermally oxidized samples are represented in Figures 4.23-26. Peakfit analysis is performed for all the graphs.

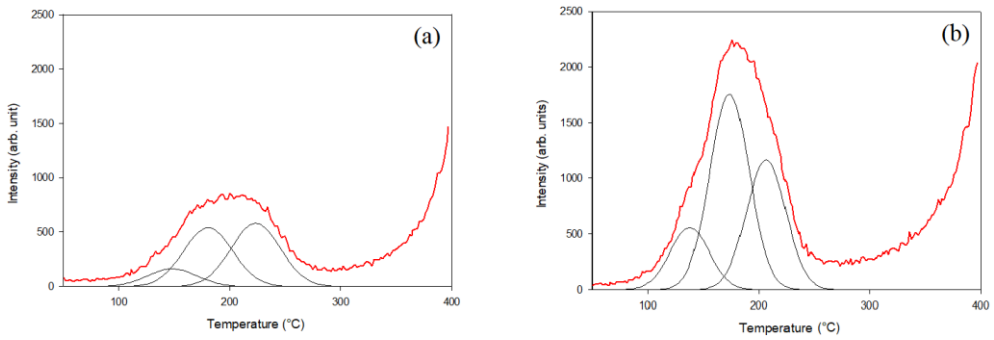


Figure 4.23 Comparative TSL spectra of (a) thermally oxidized at 160°C for 1 hour, and (b) control GUR 1020 containing 15% vitamin E.

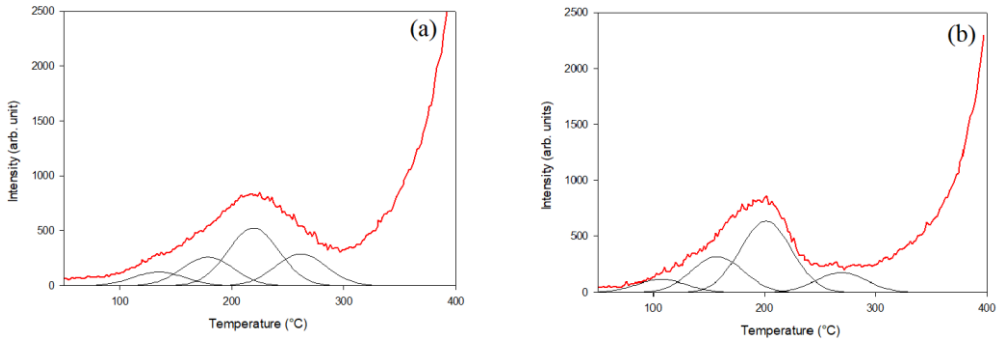


Figure 4.24 Comparative TSL spectra of (a) thermally oxidized at 160°C for 1 hour, and (b) control GUR 1020 containing 1% vitamin E.

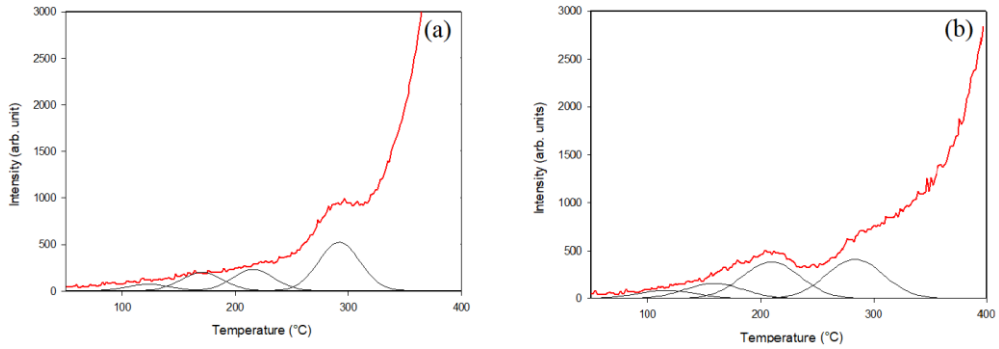


Figure 4.25 Comparative TSL spectra of (a) thermally oxidized at 160°C for 1 hour, and (b) control GUR 1020 containing 0.5% vitamin E.

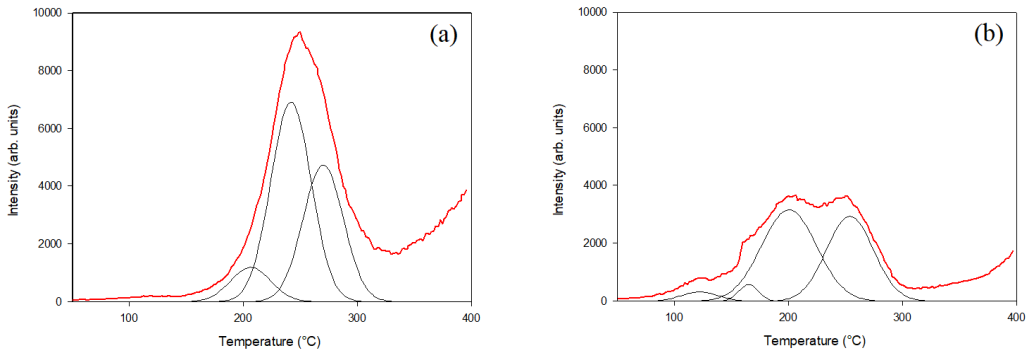


Figure 4.26 Comparative TSL spectra of (a) thermally oxidized at 160°C for 1 hour, and (b) control GUR 1050 without vitamin E.

It can be concluded from the graphs that as the concentration of vitamin E decreases the shape of TSL spectrum changes after thermal oxidation compared to control samples (no thermal oxidation performed). For 15% vitamin E samples, the shape of the spectrum does not change after thermal oxidation, but a very slight shift to higher temperature is observed. A small change in the shape of the spectrum is observed for samples with 1% vitamin E. The biggest difference in the TSL spectrum before and after thermal oxidation belong to the samples without vitamin E. For vitamin E containing samples the peakfit analysis shows that the location of the peaks does not change, and the change in the shape of spectrum is a result of the change in the intensity of different peaks. For non-vitamin E samples, both location and intensity of the peaks changes after thermal oxidation. This could be an indication that vitamin E is still active in the samples even after 10 years.

Another fact to notice is that in samples with 1% and 0.5% vitamin E and also non-vitamin E samples a peak around 280°C is observed, which is not present for 15% vitamin E

samples. The intensity of this peak increases as the concentration vitamin E decreases. It can be concluded that this peak belongs to the oxidized products and the high concentration (15%) of vitamin E prevents this peak from being appeared.

In order to investigate the behavior of TSL spectra as the time passes, the recording was continued up to one month for vitamin E containing samples. The resulting graphs are shown in Figures 4.27-30.

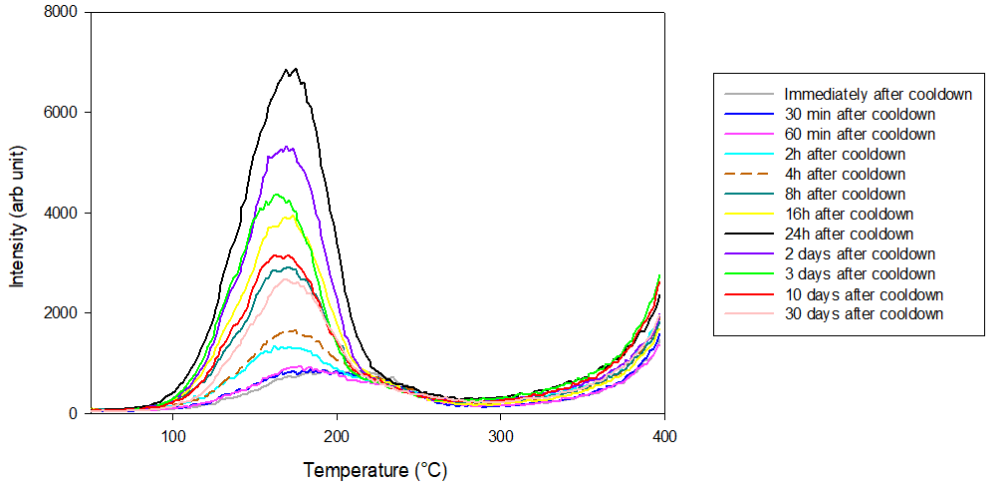


Figure 4.27 Glow curves of 15% vitamin E containing GUR 1020, Thermally oxidized at 160°C for 1 hour.

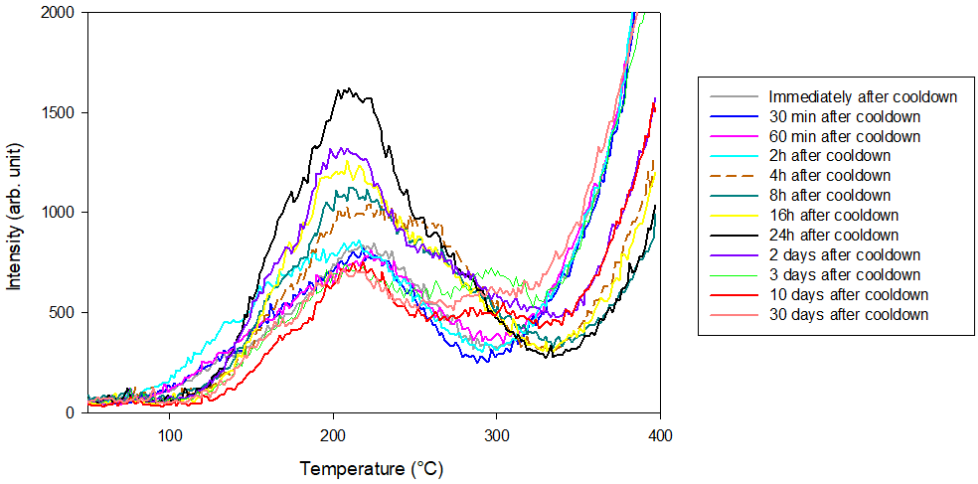


Figure 4.28 Glow curves of 1% vitamin E containing GUR 1020, Thermally oxidized at 160°C for 1 hour.

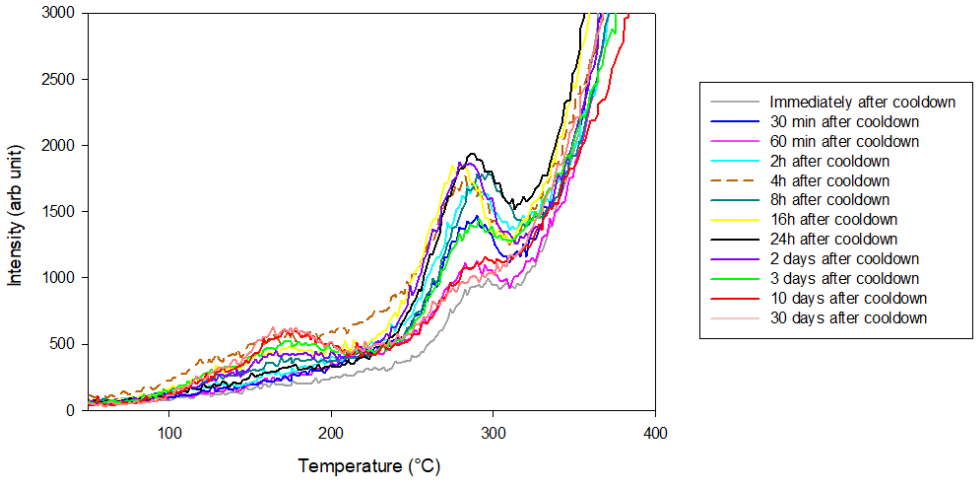


Figure 4.29 Glow curves of 0.5% vitamin E containing GUR 1020, Thermally oxidized at 160°C for 1 hour.

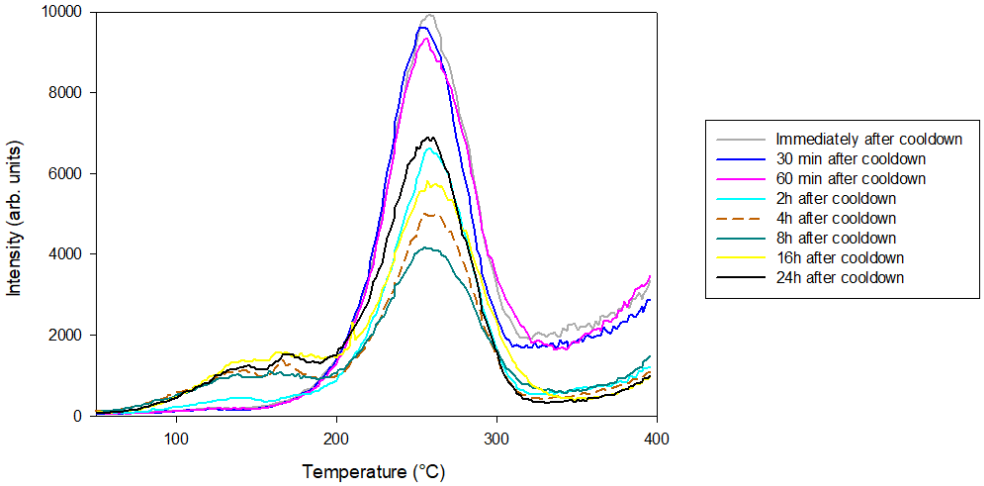


Figure 4.30 Glow curves of non-vitamin E containing GUR 1020, Thermally oxidized at 160°C for 1 hour.

The intensity of the glow curve for vitamin E containing samples behave differently from those for non-vitamin E samples. For vitamin E samples, the intensity increases as the time passes up to 24 hours after cooldown, after that the intensity decreases with time. This behavior is observed for all vitamin E containing samples with different concentrations of vitamin E. However, for non-vitamin E samples, the intensity of the glow peak behaves exactly invers. In other words, first, the intensity of the glow curve decreases up to 8 hours after cooldown and then decreases with extended aging.

The average T_m of each groups of samples have shifted to higher temperatures but the same overall glow curve shape remains. It can be inferred that extended time in air increases the temperature at which individual glow peaks luminesce.

To show the behavior of the intensity of the glow curve more clearly, the graphs of intensity vs. time are represented in Figure 4.31.

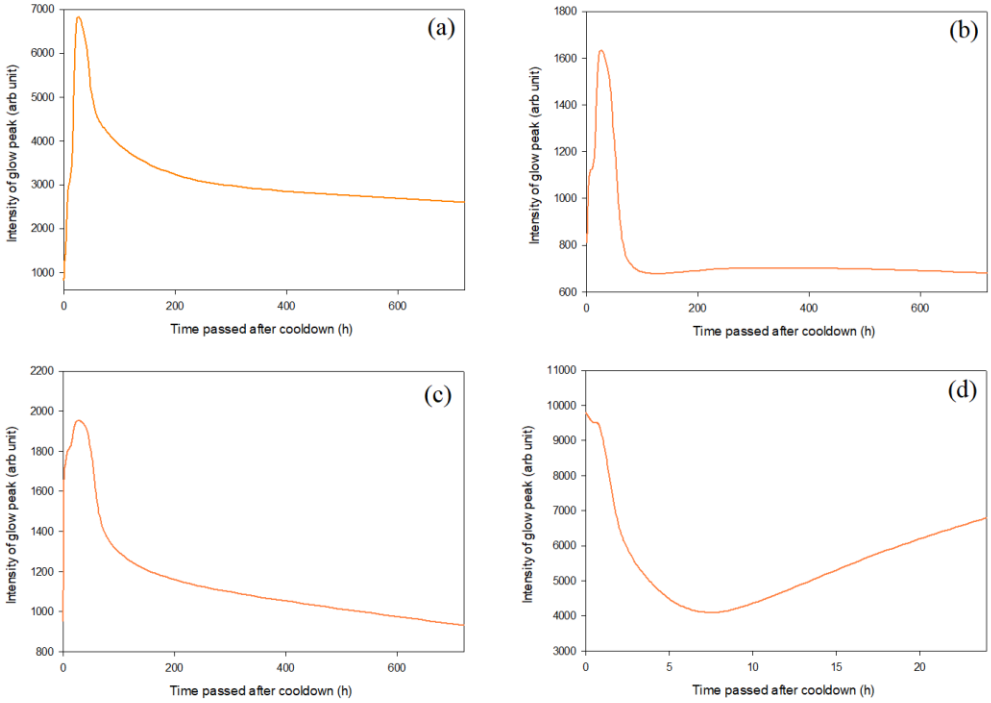


Figure 4.31 Behavior of the intensity of the glow peak as a function of time for thermally oxidized (at 160°C for 1 hour) (a) GUR 1020 containing 15% vitamin E, (b) GUR 1020 containing 1% vitamin E, (c) GUR 1020 containing 0.5% vitamin E, and (d) GUR 1050 with no vitamin E.

The intensity of the glow curve behaves the same for vitamin E containing samples as a function of time, but for non-vitamin E samples the behavior is exactly opposite. This difference is a result of the presence of vitamin E. Even a small amount of vitamin E (0.5%) can affect the behavior of the TSL spectra of the UHMWPE samples.

Chapter 5

Conclusion and Future Work

This study has investigated the long-term effects of vitamin E on free radicals and thermoluminescence properties of two grades of UHMWPE, GUR 1020 and GUR 1050. The goal of this study was to find out if a footprint of vitamin E species can be detected after 10 years of shelf-storage at room temperature.

5.1 GUR 1050 and GUR 1020, and X-ray Irradiation

The analysis of ESR spectra showed that there is a singlet in the middle of each spectrum which is an indication of OIR species. The growth rate of the intensity of this peak is much lower for vitamin E containing samples compared to non-vitamin E samples. It can be inferred from the analysis that, after irradiation, vitamin E free radicals can be detected from ESR spectra. Even though the percentage of existing free radicals a very small, their presence implies that, after even 10 years, vitamin E still is active inside the polymer.

From thermoluminescence analysis it's been concluded that two peaks were observed for X-ray irradiated non-vitamin E containing samples, one around 80°C and the other one around 260°C, which were not detected in vitamin E containing samples. However, a peak at 280°C was observed in 0.5% vitamin E containing samples, which disappears for higher concentrations of vitamin E. It could be inferred that the 260°C peak in non-vitamin E samples and 280°C peak in 0.5% vitamin E containing samples are from the same species (oxidized products), and the higher concentration of vitamin E make it disappear. Extended aging after irradiation brings out the fact that any additional peak, after irradiation, has not been detected only in vitamin E containing samples. This might be a result of the presence of vitamin E.

5.2 GUR 1020, and γ-Irradiation

The ESR spectra analysis, which were recorded 10 years after irradiation, indicate the presence of oxygen-induced polyenyle radicals in samples aged at 23°C in open air. It implies that at room temperature most of the primary radicals of GUR 1050 have been converted to the oxygen induced radicals in presence of air.

In TSL analysis four peaks were detected which are present in vitamin E containing samples. Three out of these four peaks are the same as those for X-ray irradiated samples; and one additional peak around 260°C. Another peak (around 200°C) is observed for samples with 1% and 0.5% vitamin E, which could be assigned to the concentration of vitamin E, since it's not detectable for higher percentage of vitamin E.

5.3 GUR 1050 and GUR 1020, Forced Thermal Oxidation

It can be inferred from the TSL analysis that the shape of the TSL spectrum changes after thermal oxidation and it only happens for low concentrations of vitamin E and non-vitamin E samples. In other words, as the concentration of vitamin E decreases the change in shape of the spectrum becomes more detectable.

The same as X-ray irradiated samples, a peak around 280°C is present for low concentrations of vitamin E, confirming the fact that higher percentage of vitamin E affects this peak and makes it disappear.

The graphs of intensity of the glow curve vs time indicate that any amounts of vitamin E as low as 0.5% can affect the behavior of the intensity as a function of time.

Overall results of these three sets of experiments implies that vitamin E species are active inside the polymer even after 10 years of shelf storage at room temperature.

5.4 Future Work

Future experiments could investigate the effects of X-ray irradiation duration on the free radicals behavior and thermoluminescence of the polymer. Besides the irradiation time, recording data after irradiation could be continued for a longer time.

The temperature and duration of thermal oxidation is another important factor to take into account. It would definitely have an interesting influence on the thermoluminescence of the polymer. To get more information about the effects of thermal oxidation, ESR spectroscopy is highly recommended.

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